

ALBIHNW-386

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/581333INTERNATIONAL APPLICATION NO.
PCT/SE97/02067INTERNATIONAL FILING DATES
10 December 1997

PRIORITY DATE CLAIMED

TITLE OF INVENTION POROUS MATERIAL, METHOD AND ARRANGEMENT FOR CATALYTIC
CONVERSION OF EXHAUST GASESAPPLICANT(S)
FOR DO/EO/US Edward JOBSON, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371 (c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). **(Unexecuted)**
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98; with PTO-1449, 7 references
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 & 3.31 is included.
13. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

Copy of International Application as published
Copy of International Preliminary Examination Report
Seven (7) Sheets of Formal Drawings

EXPRESS MAIL LABEL NO. EL 458418936US
DATE: June 9, 2000

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/581333

INTERNATIONAL APPLICATION NO.

PCT/SE97/02067

ATTORNEY'S DOCKET NUMBER

ALBIHNW-386

17. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

- ☒ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$970.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$840.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$970.00

Surcharge of \$130.00 for furnishing the oath or declaration later than
☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	43 - 20 =	23	x \$18.00	\$414.00	
Independent claims	2 - 3 =		x \$78.00		
MULTIPLE DEPENDENT CLAIM(s) (if applicable)			+ \$260.00	\$260.00	
TOTAL OF ABOVE CALCULATIONS =				\$1,644.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).					
SUBTOTAL =				\$1,644.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				+	
TOTAL NATIONAL FEE =				\$1,644.00	
Fee for recording the enclosed assignment (37 CFR 1.21 (h)). Assignment must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31) (\$40.00 per property).				+	
TOTAL FEES ENCLOSED =				\$1,644.00	

Amount to be:
Refunded
Charged

- a. ☐ A check in the amount of _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 12-1095 in the amount of \$1,644.00 to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to my Deposit Account No. 12-1095. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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25,428

Registration Number

06 OCT 2000

PATENT
ALBIHNW 3.3-386

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of :
Edward JOBSON et al. :
 : Group Art Unit:
International Application No. :
PCT/SE97/02067 : Examiner:
 :
International Filing Date: : Date: October 6, 2000
10 December 1997 :
 :
U.S. Application No. 09/581,333 :
 :
For: POROUS MATERIAL, METHOD AND :
ARRANGEMENT FOR CATALYTIC :
CONVERSION OF EXHAUST GASES :
X

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir: Preliminary to initiation of the prosecution of the above-identified pending U.S. patent application, the following amendments and remarks are respectfully submitted.

IN THE ABSTRACT

Please delete the original Abstract, and substitute therefor the attached revised Abstract.

IN THE SPECIFICATION

Please delete the original Specification and substitute therefor the attached revised Specification.

IN THE CLAIMS

Please delete claims 1-38 and substitute therefor the following new claims.

39. A porous material for use in the catalytic conversion of exhaust gases comprising a carrier including a first porous structure, an oxidation catalyst capable of catalyzing the oxidation of NO to NO₂ in the presence of oxygen and catalyzing the oxidation of a reducing agent, said oxidation catalyst enclosed within said first porous structure, said first porous structure including pores having dimensions such that said

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reducing agent is substantially prevented from contacting said oxidation catalyst, whereby said oxidation catalyst primarily catalyzes said oxidation of said NO to NO₂ as compared to said oxidation of said reducing agent during the catalytic conversion of said exhaust gases.

40. The porous material of claim 39 wherein said carrier includes a second porous structure, and including a reduction catalyst capable of selectively catalyzing the reduction of NO to N₂ in the presence of a reducing agent, said reduction catalyst disposed in said second porous structure, said second porous structure including pores having a dimension such that said reducing agent can contact said reduction catalyst, whereby said reduction catalyst can catalyze said reduction of NO₂ to N₂ in the presence of said reducing agent.

41. The porous material of claim 40 wherein said pores of said first porous structure are generally smaller than said pores of said second porous structure.

42. The porous material of claim 41 wherein said pores of said first porous structure have an effective size of from about 3-6 angstroms.

43. The porous material of claim 40 wherein said first and second porous structures are provided in the same layer or coating of said porous material.

44. The porous material of claim 40 wherein said first and second porous structures are provided in different layers or coatings of said porous material.

45. The porous material of claim 40 wherein said carrier including said second porous structure has been adapted to the molecular size or absorption properties of said reducing agent.

46. The porous material of claim 40 wherein the ratio of said oxidation catalyst to said reduction catalyst is

optimized, whereby said oxidation of NO to NO₂ substantially corresponds to said reduction of NO₂ to N₂.

47. The porous material of claim 40 comprising a first portion of said porous material disposed to initially receive said exhaust gas and a second portion of said porous material disposed to subsequently receive said exhaust gas, and wherein said first portion of said porous material includes more of said oxidation catalyst than said reduction catalyst and said second portion of said porous material includes more of said reduction catalyst than said oxidation catalyst.

48. The porous material of claim 40 wherein at least one of said first and second porous structures is disposed in said carrier comprising a zeolite crystal structure.

49. The porous material of claim 48 wherein said first porous structure is disposed in a carrier comprising a first zeolite and said second porous structure is disposed in a carrier comprising a second zeolite.

50. The porous material of claim 49 comprising a physical mixture of said first and second zeolites.

51. The porous material of claim 49 comprising a layered structure comprising layers of said first and second zeolites.

52. The porous material of claim 51 wherein said layers of said first and second zeolites are arranged so that said second zeolite structure will contact said exhaust gases before said first zeolite structure.

53. The porous material of claim 49 wherein said second zeolite is applied by overgrowth onto said first zeolite.

54. The porous material of claim 49 wherein the content of said oxidation catalyst in the outer layers of said first zeolite has been reduced by means of regulating the penetration depth or dispersion thereof.

55. The porous material of claim 49 including an additional crystal zeolite layer crystallized onto said first zeolite, said additional crystal zeolite layer including a reduced content of said oxidation catalyst.

56. The porous material of claim 49 wherein said first zeolite comprises crystal grains having optimized crystal grain sizes and shapes, whereby access of said reducing agent thereto is reduced and the effective oxidation of said NO to NO₂ is carried out.

57. The porous material of claim 49 wherein said first zeolite is selected from the group consisting of Ferrierite and Chabazite.

58. The porous material of claim 40 wherein said reducing agent comprises a hydrocarbon or a hydrocarbon including oxygen or sulfur.

59. The porous material of claim 40 wherein said reduction catalyst comprises an acidic zeolite catalyst.

60. The porous material of claim 40 wherein said reduction catalyst comprises a Brönstedt acid catalyst.

61. The porous material of claim 60 wherein said Brönstedt acid catalyst is selected from the group consisting of silver, copper, Rhodium, Indium, Iridium and combinations thereof.

62. The porous material of claim 39 wherein said oxidation catalyst is selected from the group consisting of platinum, palladium and mixtures thereof.

63. The porous material of claim 40 including a substrate, wherein at least one of said first and second porous structures are provided on said carrier attached to said substrate.

64. A method for the catalytic conversion of exhaust gases comprising oxidation of NO to NO₂ over an oxidation catalyst capable of oxidizing said NO to NO₂ in the presence of

oxygen and of oxidizing a reducing agent, and sterically preventing said reducing agent from contacting said oxidation catalyst, whereby said oxidation catalyst primarily catalyzes said NO to NO₂ as compared to oxidation of said reducing agent.

65. The method of claim 64 including reduction of NO to N₂ over a reduction catalyst capable of reducing said NO₂ to N₂ in the presence of said reducing agent whereby said reducing agent is at least partially consumed in order to provide a catalytically converted exhaust gas having a reduced content of NO, NO₂ and said reducing agent, and a proportionately reduced amount of N₂O and CO.

66. The method of claim 64 including adding an additional amount of said reducing agent prior to said reduction over said reduction catalyst.

67. The method of claim 66 including determining the content of said reducing agent or the amount of said NO in said exhaust gases and providing said additional amount of said reducing agent based thereon.

68. The method of claim 67 including determining the status of said catalytic conversion based on said determined amount of said reducing agent or said NO.

69. The method of claim 68 wherein said determining of said status of said catalytic conversion is carried out in a diagnostic control system.

70. The method of claim 64 including initially passing said exhaust gases through a device for storing and releasing nitrous oxides prior to said oxidation over said oxidation catalyst.

71. The method of claim 64 including initially passing said exhaust gases through a device for storing and releasing said reducing agent prior to said oxidation over said oxidation catalyst.

72. The method of claim 65 including regulating the temperature of said exhaust gases in order to ensure that said temperature is within the active temperature interval of said oxidation catalyst and said reduction catalyst.

73. The method of claim 65 including passing said at least partially catalytically converted exhaust gases over a second oxidation catalyst, whereby oxidation of residues of said reducing agent and CO can occur.

74. The method of claim 65 wherein said exhaust gases arise from an internal combustion engine, and wherein said reducing agent comprises a hydrocarbon or a hydrocarbon containing oxygen or sulfur.

75. The method of claim 74 including regulating the fuel consumption of said internal combustion engine in order to regulate the composition of said exhaust gases and to regulate the residue of nitrous oxides in said catalytically converted exhaust gases.

76. The method of claim 74 wherein said internal combustion engine comprises a diesel engine and wherein said reducing agent originates from internal combustion in said diesel engine.

77. The method of claim 76 including adding an additional amount of said reducing agent by means of a fuel injector for said diesel engine or by an injector for said additional reducing agent.

REMARKS

The above-noted cancellation of claims 1-38, and substitution of new claims 39-77, as well as the substitution of a revised Abstract and Specification, are respectfully submitted prior to initiation of the prosecution of this application in the U.S. Patent and Trademark Office.

The above-noted amendments to the claims are respectfully submitted in order to more clearly and appropriately


claim the subject matter which applicants consider to constitute their inventive contribution. No new matter is included in these amendments. In addition, a revised Abstract and Specification are submitted in order to clarify and correct the Specification and to conform it to all of the requirements of U.S. practice. No new matter is included in these amendments, and a copy of the marked-up Specification is respectfully submitted herewith in order to confirm same.

In view of the above, it is respectfully requested that these amendments now be entered, and that prosecution on the merits of this application now be initiated. If, however, for any reason the Examiner does not believe such action can be taken, it is respectfully requested that he telephone applicant's attorney at (908) 654-5000 in order to overcome any objections which he may have.

If there are any additional charges in connection with this requested amendment, the Examiner is authorized to charge applicant's Deposit Account No. 12-1095 therefor.

Respectfully submitted,

LERNER, DAVID, LITTENBERG,
KRUMHOLZ & MENTLIK, LLP



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POROUS MATERIAL, METHOD AND ARRANGEMENT
FOR CATALYTIC CONVERSION OF EXHAUST GASES

FIELD OF THE INVENTION

5

The present invention relates to a porous material for the catalytic conversion of exhaust gases. The porous material comprises a carrier with a first porous structure, and an oxidation catalyst which, in the presence of oxygen, has the ability to catalyse oxidation of nitrogen monoxide into nitrogen dioxide. The oxidation catalyst in itself also has the ability to catalyse oxidation of a reducing agent but, according to the present invention, oxidation of the reducing agent is prevented by means of the oxidation catalyst being enclosed inside the first porous structure, which has dimensions such that the reducing agent is sterically prevented from coming into contact with the oxidation catalyst.

20 Preferably, the porous material also comprises a carrier with a second porous structure and a reduction catalyst, which in the presence of the reducing agent is able to selectively catalyse reduction of nitrogen dioxide into nitrogen, whereby the reducing agent is at least partially consumed. The reduction catalyst is thereby located in the second porous structure, which has dimensions such that the reducing agent can come into contact with the reduction catalyst. The present invention also relates to a method and an arrangement which utilize the porous material, and provides for advantageous use of the porous material.

The present invention may be applied within the field of catalytic conversion of exhaust gases which originate from internal combustion engines, particularly Lean Combustion engines (LC-engines) and diesel engines.

The present invention may also be utilized for other exhaust gases, containing nitrogen oxides and having an oxygen surplus, which originate from stationary emission
5 sources such as gas turbines, power plants and the like.

BACKGROUND OF THE INVENTION

When attempting to reduce the emissions of nitrogen oxides
10 (NO_x) from internal combustion engines, many efforts have been made to modify the combustion conditions in order to reduce the NO_x -emissions, while still maintaining the combustion efficiency at a satisfactory level.

15 Among the traditional techniques used for the reduction of NO_x -emissions, inter alia, the technique of Exhaust Gas Recirculation (EGR) may be mentioned, as well as special designs of fuel injectors and combustion chambers. Other important parameters are compression, fuel injection time
20 and fuel injection pressure. Techniques involving water injection, the use of fuel/water emulsions, and so-called Selective Catalytic Reduction (SCR) by ammonia, have also been employed. It has thus been found that a one-sided optimization of the combustion efficiency often results in
25 increased NO_x -emissions.

It is presently required that both the fuel consumption and the NO_x -emissions be reduced. There are also strong demands on reduced emissions of other chemical compounds
30 which are potentially hazardous to the environment, e.g. hydrocarbons.

Accordingly, there is an increased need for catalytic converters which are also able to treat exhaust gases from
35 so-called Lean Combustion (LC) engines. Therefore, a number of different catalytic converters have been

developed and are well-known from commercial applications in e.g. motor vehicles.

Typically, conventional catalytic converters comprise one
5 or several matrices, or monolith bricks as they are
sometimes called. Such bricks or monoliths are in the form
of a ceramic honeycomb substrate, with through passages or
cells, and which can be furnished with a porous surface
coating. Particles of a suitable catalyst are embedded in
10 the surface of the matrix, and the design of the matrix
has been optimized in order to maximise the surface area
over which catalytic reactions take place. Common
catalysts are noble metals, e.g. silver (Ag), platinum
(Pt), palladium (Pd), rhodium (Rh), gallium (Ga) or
15 ruthenium (Ru) or mixtures thereof. There are also a
number of other metals and metal oxides which may be used
as catalysts. Such catalysts may have the ability to
catalyse oxidation or reduction reactions, or both.

20 It is also previously known to use crystalline aluminium
silicates, so-called zeolites, loaded with a suitable
catalyst. The use of zeolites in connection with the
catalytic conversion of exhaust gases is disclosed, e.g. in
European Application Nos. 499,931 A1 and 445,408 A.

25 Furthermore, it is also known to combine several different
catalytic matrices, or to arrange a so-called after-burner
in the catalytic conversion process. Such arrangements
are disclosed, e.g. in U.S. Patent No. 5,465,574.

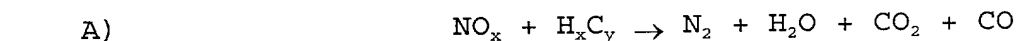
30 It is also known to use a honeycomb monolith of corrugated
metal foil, having a suitable catalyst carried or
supported on its surface.

35 It has also been suggested, e.g. in European Application
No. 483,708 A1, to combine a conventional ceramic

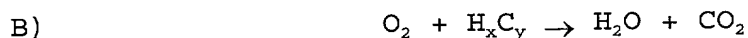
catalytic converter with an electrically heatable catalytic converter, in order to ensure that the optimum temperature for catalytic conversion is maintained.

- 5 Thus, a number of different catalyst materials, devices, and arrangements for the catalytic conversion of exhaust gases have been described in the art.

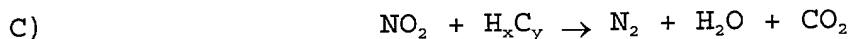
10 It is therefore believed that simultaneous elimination of nitrogen oxides (NO_x) and hydrocarbons (H_xC_y) may take place over e.g. an Ag-catalyst, according to the following (simplified) chemical reactions:



and



- 20 However, in practice, it has been found that the following reaction is predominant:



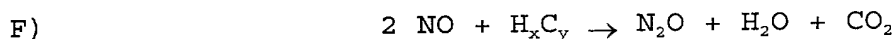
- 25 It should be noted that the term H_xC_y in these chemical reactions not only refers to hydrocarbons but is also relevant for other reducing agents which further comprise oxygen and/or sulphur. Accordingly, the reducing agent H_xC_y could also be expressed as $\text{H}_x\text{C}_y\text{O}_z\text{S}_w$. Examples of
30 reducing agents which might be present in exhaust gases are alkanes, alkenes, paraffins, alcohols, aldehydes, ketones, ethers or esters, and different sulphur-containing compounds. Also CO or H_2 could act as reducing agents. The reducing agent in the exhaust gases can
35 originate from the fuel or the combustion air, or it can

be added to the exhaust gases on purpose.

It has been found that the above-mentioned reaction according to C) is very rapid over e.g. Ag-catalysts. 5 Acidic catalysts (H^+) and acidic zeolites, doped with Ag or other suitable catalysts, have been found to be selective in the sense that NO_2 will readily be converted, whereas NO will not. This can be a great disadvantage, since NO is predominant in "lean" exhaust 10 gases from e.g. LC-engines. Another problem is that the available amount of NO_2 can become limiting for the reduction of hydrocarbons (H_xC_y) or other undesired compounds.

15 In order to solve this problem, i.e. to be able to reduce the amount of both NO and H_xC_y in the exhaust gases, it has been suggested to combine an Ag-zeolite catalyst with a Pt-catalyst.

20 Normally, the following main reactions will take place over a conventional Pt-catalyst:



When using a conventional Ag-zeolite catalyst in 30 combination with a conventional Pt-catalyst, all four reactions C), D), E) and F) will occur. However, since hydrocarbons (H_xC_y) are consumed in the chemical reactions E) and F), there is a risk that there will not be a sufficient amount of hydrocarbon (H_xC_y) left for the 35 reaction with nitrogen dioxide (NO_2), according to

reaction C). This results in an undesired residue of nitrogen dioxide (NO_2) in the catalytically converted exhaust gases, originating from reaction D).

5 Previous attempts have been made to solve this problem with different types of catalysts, by means of combining different catalysts, and by means of adding an additional amount of hydrocarbon to the exhaust gases in order to supply the reaction C) with a sufficient amount of
10 hydrocarbon.

However, many of the previous solutions have been associated with the problem of undesired oxidation of hydrocarbons (H_xC_y) over at least some surfaces of the
15 oxidation catalyst, which preferably should only catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), according to reaction D).

Another problem associated with many previously known
20 catalysts is that, during certain conditions, they will catalyse reaction F), which produces dinitrogen oxide (N_2O). This reaction is undesired, and it is preferred that the nitrogen oxides (NO_x) in the exhaust gases are converted into nitrogen (N_2) to the highest possible
25 degree, and not into dinitrogen oxide (N_2O).

Accordingly, there is a need for a new, selective oxidation catalyst material, which catalyses oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and
30 which does not catalyse oxidation of hydrocarbons.

Furthermore, there is also a need for an effective combination of such a selective oxidation catalyst material, catalysing a reaction which produces nitrogen
35 dioxide (NO_2), and a reduction catalyst material, catalysing a reaction in which nitrogen dioxide (NO_2) is

reduced by hydrocarbons or other reducing agents into nitrogen (N_2).

Accordingly, one object of the present invention is to
5 provide a porous material for catalytic conversion of
exhaust gases, by means of which porous material it is
possible to selectively catalyse the oxidation of nitrogen
monoxide (NO) into nitrogen dioxide (NO_2), and avoid
catalytic oxidation of hydrocarbons (H_xC_y) or other
10 reducing agents.

A second object of the present invention is to provide a
porous material for catalytic conversion of exhaust
gases, wherein primarily only the desired reactions take
15 place, as is a result of which the contents of NO, NO_2
and H_xC_y in the catalytically converted exhaust gases are
effectively decreased, and the resulting conversion
products primarily are N_2 , CO_2 and H_2O , and not N_2O .

20 A third object of the present invention is to provide a
method for the catalytic conversion of exhaust gases in
which such a porous material is utilized.

A fourth object of the present invention is to provide an
25 advantageous use of porous materials therefore.

A fifth object of the present invention is to provide an
advantageous arrangement for the catalytic conversion of
exhaust gases utilizing such a porous material.

30

SUMMARY OF THE INVENTION

In accordance with the present invention these and other
objects have now been realized. In accordance with the
present invention a porous material has been discovered
35 for use in the catalytic conversion of exhaust gases
comprising a carrier including a first porous structure,

an oxidation catalyst capable of catalyzing the oxidation of NO to NO₂ in the presence of oxygen and catalyzing the oxidation of a reducing agent, the oxidation catalyst enclosed within the first porous structure, the first
5 porous structure including pores having dimensions such that the reducing agent is substantially prevented from contacting the oxidation catalyst, whereby the oxidation catalyst primarily catalyzes the oxidation of the NO to NO₂ as compared to the oxidation of the reducing agent
10 during the catalytic conversion of the exhaust gases. In accordance with a preferred embodiment the carrier includes a second porous structure, and including a reduction catalyst capable of selectively catalyzing the reduction of NO to N₂ in the presence of a reducing
15 agent, the reduction catalyst disposed in the second porous structure, the second porous structure including pores having a dimension such that the reducing agent can contact the reduction catalyst, whereby the reduction catalyst can catalyze the reduction of NO₂ to N₂ in the
20 presence of the reducing agent.

In accordance with a preferred embodiment of the porous material of the present invention the pores of the first porous structure are generally smaller than the pores of
25 the second porous structure. Preferably, the pores of the first porous structure have an effective size of from about 3-6 angstroms.

In accordance with another embodiment of the porous
30 material of the present invention the first and second porous structures are provided in the same layer or coating of the porous material.

In accordance with another embodiment of the porous
35 material of the present invention the first and second porous structures are provided in different layers or

coatings of the porous material.

In accordance with another embodiment of the porous material of the present invention the carrier including
5 the second porous structure has been adapted to the molecular size or absorption properties of the reducing agent.

In accordance with another embodiment of the porous
10 material of the present invention the ratio of the oxidation catalyst to the reduction catalyst is optimized, whereby the oxidation of NO to NO₂ substantially corresponds to the reduction of NO₂ to N₂.

15 In accordance with another embodiment of the porous material of the present invention the porous material includes a first portion of the porous material disposed to initially receive the exhaust gas and a second portion of the porous material disposed to subsequently receive
20 the exhaust gas, and wherein the first portion of the porous material includes more of the oxidation catalyst than the reduction catalyst and the second portion of the porous material includes more of the reduction catalyst than the oxidation catalyst.

25 In accordance with another embodiment of the porous material of the present invention at least one of the first and second porous structures is disposed in the carrier comprising a zeolite crystal structure.
30 Preferably the first porous structure is disposed in a carrier comprising a first zeolite and the second porous structure is disposed in a carrier comprising a second zeolite. In a preferred embodiment the porous material comprises a physical mixture of the first and second
35 zeolites.

In accordance with another embodiment of the porous material of the present invention, the porous material comprises a layered structure comprising layers of the first and second zeolites. Preferably, the layers of the first and second zeolites are arranged so that the second zeolite structure will contact the exhaust gases before the first zeolite structure.

In accordance with another embodiment of the porous material of the present invention the second zeolite is applied by overgrowth onto the first zeolite.

In accordance with another embodiment of the porous material of the present invention the content of the oxidation catalyst in the outer layers of the first zeolite has been reduced by means of regulating the penetration depth or dispersion thereof.

In accordance with another embodiment of the porous material of the present invention the porous material includes an additional crystal zeolite layer crystallized onto the first zeolite, the additional crystal zeolite layer including a reduced content of the oxidation catalyst.

In accordance with another embodiment of the porous material of the present invention the first zeolite comprises crystal grains having optimized crystal grain sizes and shapes, whereby access of the reducing agent thereto is reduced and the effective oxidation of the NO to NO₂ is carried out.

In accordance with another embodiment of the porous material of the present invention the first zeolite is Ferrierite or Chabazite.

In accordance with another embodiment of the porous

material of the present invention the reducing agent is a hydrocarbon or a hydrocarbon including oxygen and/or sulfur.

5 In accordance with another embodiment of the porous material of the present invention the reduction catalyst comprises an acidic zeolite catalyst, preferably a Brönstedt acid catalyst, such as silver, copper, Rhodium, Indium, Iridium or combinations thereof.

10

In accordance with another embodiment of the porous material of the present invention the oxidation catalyst is platinum, palladium or mixtures thereof.

15 In accordance with another embodiment of the porous material of the present invention the porous material includes a substrate, wherein at least one of the first and second porous structures are provided on the carrier attached to the substrate.

20

In accordance with the present invention a method has also been provided for the catalytic conversion of exhaust gases comprising oxidation of NO to NO₂ over an oxidation catalyst capable of oxidizing the NO to NO₂ in
25 the presence of oxygen and of oxidizing a reducing agent, and sterically preventing the reducing agent from contacting the oxidation catalyst, whereby the oxidation catalyst primarily catalyzes the NO to NO₂ as compared to oxidation of the reducing agent.

30

In a preferred embodiment, the method includes reduction of NO to N₂ over a reduction catalyst capable of reducing the NO₂ to N₂ in the presence of the reducing agent, whereby the reducing agent is at least partially consumed
35 in order to provide a catalytically converted exhaust gas having a reduced content of NO, NO₂ and the reducing

agent, and a proportionately reduced amount of N_2O and CO .

In accordance with one embodiment of the method of the present invention the method includes adding an additional amount of the reducing agent prior to the reduction over the reduction catalyst. Preferably, the method includes determining the content of the reducing agent or the amount of the NO in the exhaust gases and providing the additional amount of the reducing agent based thereon. In a preferred embodiment the method includes determining the status of the catalytic conversion based on the determined amount of the reducing agent or the NO . Preferably, determining of the status of the catalytic conversion is carried out in a diagnostic control system.

In accordance with one embodiment of the method of the present invention the method includes initially passing the exhaust gases through a device for storing and releasing nitrous oxides prior to the oxidation over the oxidation catalyst.

In accordance with another embodiment of the method of the present invention the method includes initially passing the exhaust gases through a device for storing and releasing the reducing agent prior to the oxidation over the oxidation catalyst.

In accordance with another embodiment of the method of the present invention the method includes regulating the temperature of the exhaust gases in order to ensure that the temperature is within the active temperature interval of the oxidation catalyst and the reduction catalyst.

In accordance with another embodiment of the method of

the present invention the method includes passing the at least partially catalytically converted exhaust gases over a second oxidation catalyst, whereby oxidation of residues of the reducing agent and CO can occur.

5

In accordance with another embodiment of the method of the present invention the exhaust gases arise from an internal combustion engine, and the reducing agent comprises a hydrocarbon or a hydrocarbon containing
10 oxygen or sulfur. Preferably, the method includes regulating the fuel consumption of the internal combustion engine in order to regulate the composition of the exhaust gases and to regulate the residue of nitrous oxides in the catalytically converted exhaust gases.

15

In accordance with another embodiment of the method of the present invention the internal combustion engine comprises a diesel engine and the reducing agent originates from internal combustion in the diesel engine.

20 Preferably, the method includes adding an additional amount of the reducing agent by means of a fuel injector for the diesel engine or by an injector for the additional reducing agent.

25 Thus, the first object of the present invention is achieved by means of a porous material for catalytic conversion of exhaust gases which comprises a carrier with a first porous structure, and an oxidation catalyst. In the presence of oxygen, the oxidation catalyst has the
30 ability to catalyse oxidation of nitrogen monoxide into nitrogen dioxide, according to a first reaction. Furthermore, the oxidation catalyst in itself has the ability to catalyse oxidation of a reducing agent, according to a second reaction. According to the present
35 invention, the oxidation catalyst is enclosed inside the porous structure, which has dimensions such that the

reducing agent is sterically prevented from coming into contact with the oxidation catalyst. This will enable primarily the first reaction, out of said first and second reactions, to take place over the oxidation catalyst
5 during the catalytic conversion of the exhaust gases.

The second object of the present invention is achieved by means of a porous material which further comprises a carrier with a second porous structure and a reduction
10 catalyst. In the presence of a reducing agent, the reduction catalyst is able to selectively catalyse reduction of nitrogen dioxide into nitrogen, according to a third reaction, whereby the reducing agent participates in the third reaction and is at least partially consumed.
15 Thereby, the reduction catalyst is located in the second porous structure, which has dimensions such that the reducing agent can come into contact with the reduction catalyst in order to enable the third reaction to take place.

20 The third object of the present invention is achieved by means of a method for catalytic conversion of exhaust gases which comprises oxidation of nitrogen monoxide into nitrogen dioxide over an oxidation catalyst, according to
25 a first reaction, whereby the oxidation catalyst also has the ability to, according to a second reaction, catalyse oxidation of a reducing agent. According to the present invention, however, the reducing agent is sterically prevented from coming into contact with the oxidation
30 catalyst, as a result of which primarily the first reaction, out of said first and second reactions, takes place over the oxidation catalyst.

In accordance with the present invention, the fourth
35 object is achieved by the use of a porous material according to the present invention, providing functions

both for the oxidation of nitrogen monoxide into nitrogen dioxide and for the reduction of nitrogen dioxide into nitrogen, for catalytic conversion of exhaust gases which have an oxygen surplus.

5

In accordance with the present invention, the fifth object of the present invention is achieved by an arrangement, for catalytic conversion of exhaust gases from an internal combustion engine, comprising a porous material according to the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more fully appreciated with reference to the following detailed description, which refers to the attached drawings and graphs, in which:

Fig. 1 is schematic representation of a portion of a porous material according to the present invention, showing an enlarged view as seen from inside a pore in the porous material. The major chemical reactions which occur during the catalytic conversion of exhaust gases are also indicated;

Fig. 2 is a side, perspective, schematic representation of one embodiment of the porous material according to the present invention, with an enlarged detailed view of a portion of the porous material including a supporting substrate;

30

Fig. 3A is a schematic representation of an enlarged detailed view of a portion of the enlarged detailed view shown in Fig. 2, depicting a variant of the porous material according to the present invention, comprising a physical mixture of two different zeolite carriers;

Fig. 3B is a schematic representation of another enlarged detailed view of a portion of the enlarged detailed view shown in Fig. 2, depicting another variant of the porous material according to the present invention, comprising a
5 layered structure of two different zeolite carriers;

Fig. 3C is a schematic representation of an alternative to the layered structure in Fig. 3B;

10 Fig. 4A is a side, perspective, schematic representation of an embodiment of a porous material according to the present invention, having a first portion and a second portion;

15 Fig. 4B is a side, perspective, schematic representation of another embodiment of the present invention, wherein the porous material according to the present invention comprises two separate, different parts, intended to be used together in a single catalytic conversion process;

20 Fig. 5 is a side, elevational, schematic process diagram of an arrangement for catalytic conversion of exhaust gases according to the present invention;

25 Graph 1A is a graphical representation of results from a laboratory evaluation of a porous sample, comprising a physical mixture of Pt-Ferrierite and Ag-Ferrierite, when a linear hydrocarbon is supplied in the gas which is to be catalytically converted;

30 Graph 1B is a graphical representation of results from a laboratory evaluation of the same porous sample as in Graph 1A, but when a branched hydrocarbon is supplied in the gas which is to be catalytically converted;

35 Graph 2A is a graphical representation of results from a

laboratory evaluation of a porous material according to the present invention, comprising a physical mixture of Pt-Ferrierite and Ag-Mordenite, when a linear hydrocarbon is supplied in the gas which is to be catalytically
5 converted; and

Graph 2B is a graphical representation of results from a laboratory evaluation of the same porous material according to the present invention as in Graph 2A, but
10 when a branched hydrocarbon is supplied in the gas which is to be catalytically converted.

DETAILED DESCRIPTION

15 In the following detailed description, a porous material according to the present invention will be described with reference to the attached drawings.

The porous material 1 in Fig. 1 comprises a carrier with a
20 first porous structure 2, 2'. An oxidation catalyst (OX) is enclosed inside the first porous structure 2, 2'. In the presence of oxygen (O_2), the oxidation catalyst (OX) has the ability to catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), according to a first
25 reaction 3. Furthermore, the oxidation catalyst (OX) in itself has the ability to catalyse oxidation of a reducing agent (HC), according to a second reaction (not present in Fig. 1).

30 According to the present invention, however, oxidation of the reducing agent according to the second reaction is not desired, since the reducing agent (HC) is more useful in a third reaction, as will become apparent below.

35 In order to prevent the undesired second reaction from occurring, the oxidation catalyst (OX) is enclosed inside

the first porous structure 2, 2', which has dimensions such that the reducing agent (HC) is sterically prevented, 4, 4', from coming into contact with the oxidation catalyst (OX). This will enable primarily the desired
5 first reaction 3, out of said first and second reactions, to take place over the oxidation catalyst (OX) during the catalytic conversion of exhaust gases. In this context, the term "first porous structure" primarily refers to internal micro-pores in the carrier material or micro-
10 pores between carrier particles or grains.

Preferably, the porous material 1 further comprises a carrier with a second porous structure 5, 5', in which a reduction catalyst (RED) is located. In this context, the
15 term "second porous structure" can include internal micro-pores in the carrier material, or cavities or channels between carrier particles, but also cavities inside or channels through the porous material, i.e. macro-pores. In the presence of a reducing agent (HC), the reduction
20 catalyst (RED) is able to selectively catalyse reduction of nitrogen dioxide (NO_2) into nitrogen (N_2), according to a third reaction 6, shown schematically in Fig. 1. Thereby, the reducing agent (HC) participates in the third reaction 6 and is at least partially consumed.

25 According to the present invention, the reduction catalyst (RED) is located in the second porous structure 5, 5', which has dimensions such that the reducing agent (HC) can come into contact with the reduction catalyst (RED). This
30 enables the desired third reaction 6 to take place during the catalytic conversion of exhaust gases.

According to one embodiment of the porous material according to the present invention, the first porous
35 structure 2, 2' on an average exhibits smaller entrances 7 for the reducing agent (HC) than the second porous

structure 5, 5'. In this manner, the reducing agent (HC) is prevented from coming into contact with the oxidation catalyst (OX), enclosed inside the first porous structure 2, 2', but is not prevented from coming into contact with
5 the reduction catalyst (RED) in the second porous structure 5, 5'. The pores in the first porous structure 2, 2' should preferably primarily have an effective size of from about 3 to 6 Å.

10 According to another embodiment of the porous material, both the first 2, 2' and the second 5, 5' porous structures are provided in the same layer or coating of the porous material.

15 If desired, however, the first 2, 2' and the second 5, 5' porous structures can be provided in different layers/coatings of the porous material. This might be an advantage, depending on the composition of the exhaust gases which are to be catalytically converted.

20 In one embodiment of the porous material, the carrier with the second porous structure 5, 5' is adapted to the molecule size and/or the adsorption properties of the reducing agent (HC) or agents, which is/are expected to
25 occur in the exhaust gases.

In another embodiment of the porous material, the ratio between the oxidation catalyst (OX) and the reduction catalyst (RED) has been optimized so that the production
30 of nitrogen dioxide (NO₂), according to the first reaction 3, essentially corresponds to the consumption of nitrogen dioxide (NO₂), according to the third reaction 6.

In still another embodiment of the present invention (Fig. 35 4A), the porous material further comprises a first portion 10 and a second portion 11, wherein the first portion 10

is intended to receive exhaust gases 12 before the second portion 11 during the catalytic conversion. Thereby, the first portion 10 contains a larger quantity of the oxidation catalyst (OX) than the second portion 11, 5 whereas the second portion 11 contains a larger quantity of the reduction catalyst (RED) than the first portion 10. Accordingly, in a flow of exhaust gases the first reaction 3, producing NO_2 , will take place upstream the third reaction 6, which consumes NO_2 . As shown in Fig. 4B, it 10 also conceivable with embodiments wherein the first and second portions are separated from each other, as long as they used for catalytic conversion in the same conversion process.

15 According to one embodiment of the porous material, the first 2, 2' and/or the second 5, 5' porous structure is provided in a carrier which is a zeolite crystal structure.

20 Furthermore, both the first 2, 2' and the second 5, 5' porous structures can be provided in carriers of zeolite type, wherein preferably the first porous structure 2, 2' is provided in a first zeolite 14 and the second porous structure in a second zeolite 15.

25 As earlier mentioned, according to the present invention, the first porous structure 2, 2' and, accordingly, also the first zeolite 14 should provide suitable properties in order to prevent the earlier-mentioned, undesired second 30 reaction from taking place.

There are a number of different ways of combining different zeolites in a porous material according to the present invention. Accordingly, the porous material can 35 comprise a physical mixture 13 of the first zeolite 14 and the second zeolite 15 (Fig. 3A).

Furthermore, the porous material can comprise a layered structure, 16 and 17, of the first zeolite and the second zeolite (Figs. 3B and 3C). Different layers may also be
5 applied or coated onto different supporting substrates 18 or different surfaces of a substrate 18.

In certain applications, it may be preferred to arrange the layered structure 17 so that, in a flow of exhaust
10 gases, the second zeolite will encounter the exhaust gases before the first zeolite. This might be the case e.g. when the exhaust gases which are to be converted contain a proportionately high content of NO_2 but a low content of NO .

15 In other applications, e.g. when the content of NO in the exhaust gases is proportionately high but the content of NO_2 is low, it might be desirable to arrange the layered structure 16 in the opposite way, i.e. the first zeolite
20 outside the second zeolite.

According to one embodiment of the porous material, a layered structure is achieved by means of the second zeolite 15, which provides the second porous structure 5,
25 5', being crystallized onto the first zeolite 14, which provides the first porous structure 2, 2'. This can be done by means of so-called over-growth.

Another embodiment of the porous material aims at further
30 reducing the occurrence of the earlier-mentioned, undesired second reaction. In this embodiment, the content of oxidation catalyst (OX) has been reduced in the outer layers 8 of the first zeolite by means of partial ion-exchange (indicated in Fig. 1). Methods for altering the
35 penetration depth and dispersion of the catalytically active metals are well-known to the skilled person and

will not be described in any greater detail.

In another embodiment of the porous material, an additional zeolite crystal layer with a reduced content of oxidation catalyst (OX) is crystallized onto the first zeolite, by means of so-called over-growth. Thereby, the additional layer advantageously comprises a zeolite which provides a porous structure with even smaller pores/entrances than the first zeolite. In this manner, undesired reducing agent can more effectively be prevented from getting inside the internal pore structure of the first zeolite, at the same time as the nitrogen oxide (NO) will be admitted and can move freely inside said internal pore structure.

Also, the dimensions of the crystal grains in the zeolite crystal structures can be used in order to facilitate desired chemical reactions, and in order to prevent undesired chemical reactions. Different crystal structures can be achieved in several different ways, e.g. by means of the choice of the crystallization conditions and the choice of zeolite type. Also, the internal pore structure of the zeolites is influenced by the choice of zeolite type.

Thus, according to one embodiment of the porous material, the size and shape of the crystal grains in the crystal structure of the first zeolite, has been optimized both in order to prevent access for the reducing agent (HC), and in order to allow oxidation of NO to NO₂. The optimization of the grain size is important since it makes it possible to maximise the oxidation of NO into NO₂, and to minimize the oxidation of HC.

In another embodiment of the porous material, a proportionately small pore size, in the crystal structure

of the first zeolite which provides the first porous structure 2, 2', has been achieved by means of selecting a Ferrierite-zeolite or a Chabazite-zeolite, and not e.g. a Mordenite-zeolite.

5

As earlier mentioned, the porous material according to the present invention has the ability to catalyse oxidization of nitrogen monoxide (NO) into nitrogen dioxide (NO₂), and preferably also the ability to selectively catalyse
10 reduction of nitrogen dioxide (NO₂) into nitrogen (N₂) in the presence of a reducing agent (HC). Thereby, the reducing agent (HC) may be any suitable reducing agent which is present in, or added to, the exhaust gases which are to be catalytically converted.

15

It is an advantage, however, if the reducing agent (HC) in the exhaust gases is a hydrocarbon (H_xC_y) or a chemical compound comprising oxygen and sulphur (H_xC_yO_zS_w). These compounds can originate from the fuel which is combusted
20 and will, as earlier mentioned, be at least partially consumed according to the earlier-mentioned third reaction 6 over the reduction catalyst (RED). Alternative fuels, e.g. rape methyl ether, may produce oxygen-containing compounds, whereas sulphur is frequently present in most
25 fuels.

The reduction catalyst (RED) in the second porous structure 5, 5' might be of any suitable, previously known type. However, in the porous material according to the
30 present invention, the reduction catalyst (RED) preferably comprises Brönstedt acid sites, and silver (Ag), copper (Cu) or Rhodium (Rh), Cobalt (Co), Indium (In), Iridium (Ir) or combinations thereof. In the porous material according to the present invention, acidic zeolite
35 catalysts are preferred as reduction catalysts (RED) .

The oxidation catalyst (OX) may be of any type suitable for the purpose, but preferably comprises platinum (Pt) and/or Palladium (Pd).

5 The herein used term "porous material" should be regarded as including the entire structure/mass which might be present inside a unit for the catalytic conversion of exhaust gases. Accordingly, the term "porous" should be understood both in a microscopic and in a macroscopic
10 sense, i.e. the porous material could comprise elements which in themselves are not porous to exhaust gases. However, the material structure as a whole, i.e. the "porous material" according to the present invention, will allow the exhaust gases which are to be catalytically
15 converted to pass through. It should also be noted that embodiments wherein the porous material is composed of several separated parts, having different structures and functions, are conceivable, as long as they are used in the same catalytic conversion process.

20 The porous material, according to the present invention, may be coated onto one or several suitable substrates 18 or matrixes in order to provide a carrier or several carriers which comprise the first or/and the second porous
25 structures. Suitable substrates for this purpose are well-known from the prior art, and will not be described in any greater detail, especially since they are of minor importance for the present invention.

30 Accordingly, the substrate 18 may be a metal substrate of a previously known type. The substrate 18 may also be a supporting, previously known, honeycomb structure of a suitable material, with or without catalytic activity.

35 It should also be noted that the term "porous structure" used herein should be understood as to include both micro-

pores and macro-pores of the porous material. Accordingly, internal micro-pores, cavities between carrier particles, channels inside or through the porous material, etc., are all included within the scope of "porous structure".

5

For instance, there is no need for the second porous structure 5, 5 to be an internal micro-pore structure inside a carrier material, but the second porous structure 5, 5' could instead be provided by a more open, macroscopic structure. The first porous structure 2, 2', however, is preferably an internal micro-structure inside a carrier material, in order to provide sufficient sterical hindrance against the admittance of the (undesired) reducing agent into the sites where the oxidation catalyst is situated.

In the following discussion, a method for catalytic conversion of exhaust gases, according to the present invention, will be described in greater detail with reference to the attached Figs. 1 and 5. The method according to the present invention comprises oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO₂) over an oxidation catalyst (OX), according to a first reaction 3 (Fig. 1). The oxidation catalyst (OX) in itself has the ability to catalyse oxidation of a reducing agent (HC), according to a second reaction (not present in Fig. 1). According to the present invention, however, the reducing agent (HC) is sterically prevented 4, 4' from coming into contact with the oxidation catalyst (OX). As a result of this, primarily the first reaction 3, out of the first and second reactions, takes place over the oxidation catalyst (OX).

According to one embodiment of the present invention, the method further comprises reduction of nitrogen dioxide (NO₂) into nitrogen (N₂) over a reduction catalyst (RED)

in the presence of a reducing agent (HC), according to a third reaction 6. Thereby, the reducing agent (HC) participates in the third reaction 6 and is at least partially consumed. In this way, catalytically converted exhaust gases 12' (Fig. 5), having a reduced content of nitrogen monoxide (NO), nitrogen dioxide (NO₂) and reducing agent (HC) and a proportionately low content of dinitrogen oxide (N₂O), are obtained. Furthermore, the converted exhaust gases will have a reduced content of carbon monoxide (CO).

When desirable, an additional amount, 19, 19', or 19'', of reducing agent (HC) can be added with a suitable injection device 28, before reduction takes place over the reduction catalyst (RED), according to the third reaction 6 (Figs. 1 and 5). In this manner, the stoichiometrics of the occurring chemical reactions can be influenced so that the catalytic conversion becomes as complete as possible. In internal combustion engines, it is also possible to increase or regulate the amount of available reducing agent by means of so-called engine parameter tuning. This can be done by e.g. fuel injection timing, valve timing, post-injection, control of charging pressure and/or fuel injection pressure, EGR, transmission ratio, etc.

Advantageously, the additional amount, 19, 19', or 19'', of reducing agent (HC) can be regulated on the basis of a measured or previously mapped content of reducing agent (HC) and/or nitrogen oxides (NO_x) in the exhaust gases 12, 12'.

The measured content of reducing agent (HC) or nitrogen oxides (NO_x) in the catalytically converted exhaust gases (12') can also be used in a diagnostic control system 22, providing an indication of the status of the catalytic conversion.

The exhaust gases 12 can also be passed through a device having the ability to store and when necessary release nitrogen oxides (NO_x) before oxidation over the oxidation catalyst (OX), according to the first reaction 3. Such NO_x -absorbers are well-known to the person skilled in the art, and will not be described in any greater detail herein. Before the oxidation, the exhaust gases 12 can also be passed through a previously known device having the ability to store, and when necessary release, reducing agent (HC), e.g. hydrocarbon. This embodiment is useful for e.g. cold starts of an internal combustion engine.

In order to ensure that the oxidation catalyst (OX) and/or the reduction catalyst (RED) is functioning in the best possible way, i.e. are within an active temperature interval, the temperature of the exhaust gases can be regulated before the passage through the porous material 21 according to the present invention. This can be done with any previously known device 23 which is suitable for the purpose.

In order to further improve the catalytic conversion, the exhaust gases can be allowed to pass a second oxidation catalyst 24, over which oxidation of residues of reducing agent and/or carbon monoxide can take place. In this way, it is ensured that the exhaust gases, which have been at least partially catalytically converted over the porous material 21, reach a sufficiently high degree of catalytic conversion.

It is advantageous for the method of the present invention if the exhaust gases 12 originate from an internal combustion engine 25, and the reducing agent (HC) comprises a hydrocarbon (H_xC_y) and/or a chemical compound ($\text{H}_x\text{C}_y\text{O}_z\text{S}_w$) further comprising oxygen and/or sulphur.

Furthermore, the fuel 26 consumption of the internal combustion engine 25 will influence the chemical composition of the exhaust gases 12. Legislative
5 regulations are imposed both on fuel consumption and the residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases 12'. In one embodiment of the present invention, both the fuel consumption of the internal combustion engine, and the
10 residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases 12', are regulated in order to fulfil the relevant legislative regulations.

In one preferred embodiment of the method according to the
15 present invention, the internal combustion engine 25 is a diesel engine and the reducing agent (HC) originates from internal combustion in said diesel engine.

When diesel engines are concerned, an additional amount 19
20 of reducing agent (HC) can advantageously be supplied to the engine via a fuel injector of the diesel engine and/or via a separate injector for additional reducing agent.

It is preferred to use a porous material according to the
25 present invention, for catalytic conversion of exhaust gases 12, which have an oxygen surplus and, accordingly, are difficult to convert in conventional catalytic converters, e.g. three-way converters. In such use, the porous material provides functions both for the oxidation
30 of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and for the reduction of nitrogen dioxide (NO_2) into nitrogen (N_2).

It is also preferred with an arrangement 27, according to
35 the present invention, for catalytic conversion of exhaust gases which originate from an internal combustion engine

25. Thereby, the arrangement comprises a porous material
21 according to the present invention or, furthermore,
operates through a method according to the present
invention.

5

EXAMPLE

In order to more clearly illustrate the basic principles
of the present invention, a number of porous samples, i.e.
10 model catalyst materials, were produced in a series of
laboratory trials.

In the laboratory trials, zeolites of the basic types
Mordenite, Ferrierite and Chabazite were used in order to
15 provide catalyst carriers.

The different zeolite types had the following channel/pore
dimensions:

20 Mordenite: free diameter: 12 rings 6.5 x 7.0 Å
8 rings 2.6 x 5.7 Å

Ferrierite: free diameter: 10 rings 4.2 x 5.4 Å
8 rings 3.5 x 4.8 Å

25

Chabazite: free diameter: 8 rings 3.8 x 3.8 Å

As evident from above, the selected zeolites had either 8
rings, 10 rings or 12 rings, providing entrances into
30 their internal micro-pore structure. The selected zeolite
raw materials were provided in the form of NH₄-zeolites.

Preparation of platinum-zeolites (Pt):

35 Samples of the different NH₄-zeolites were calcined during
1 hour at 500°C under oxygen flow in order to transfer the

zeolites into acidic form, i.e into H-zeolites. Amounts of 0.5 wt-%, 1.0 wt-% or 1.5 wt-% of platinum (PT) were loaded onto the H-zeolites by means of contacting them with an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$. Thereby, the
5 0.01 M Pt-solution was added dropwise to zeolite dispersed in water. The obtained mixtures were stirred during 24 hours at room temperature, filtered, washed with H_2O , and dried overnight at 60°C . Thereafter, the samples were calcined during 2 hours at 450°C in dry air, with a rate
10 of $0.5^\circ\text{C} \times \text{min}^{-1}$, whereafter the samples were cooled down in a N_2 -flow.

Methods for Pt-loading are described in greater detail in the publications J. Catal. 113 (1988), p. 220-235 (Tzou et
15 al.) and J. Catal. 117 (1989), p. 91-101 (Homeyer et al.).

Preparation of silver-zeolite (Ag):

Ag-zeolites were produced by loading 5 wt-% Ag onto the
20 different NH_4 -zeolites by means of impregnation with AgNO_3 , using the so-called "incipient wetness" method. Thereby, the metal salt (AgNO_3) was dissolved in a minimum of water (1 ml/gram of zeolite), whereafter the obtained solution was mixed with the zeolite powders. Finally, the
25 samples were calcined during 16 hours at 550°C in a muffle furnace and stored in the dark until evaluation took place.

Evaluation of catalytic conversion efficiency:

30

Before the evaluation, the obtained Pt-zeolites and Ag-zeolites, and physical mixtures of these, were compressed into pellets, i.e. model porous samples, and the catalytic conversion efficiency of the different porous samples was
35 evaluated.

In the prepared porous samples, the Pt-zeolites were intended to provide the earlier-mentioned NO-oxidation function, whereas the Ag-zeolites were intended to provide the earlier-mentioned NO₂-reduction function.

5

The evaluation of the catalytic conversion efficiency was performed by means of inserting a small amount (0.3 ml) of porous sample, into a device suitable for the purpose of evaluating catalytic conversion efficiency. Thereafter, a
10 gas flow of 300 ml/min, with the composition 500 ppm NO, 350 ppm C₈H₁₈, 6% O₂, 12% H₂O, 10% CO₂ and 350 ppm CO, was passed through the sample chamber in which the porous material sample was placed. The temperature was increased step-wise from 140 to 500°C, while the composition of the
15 catalytically converted exhaust gases from the sample chamber was detected.

The catalytic conversion efficiency for some of the different porous samples, comprising the different
20 zeolites and physical mixtures of these, is evident from Table 1 below. Table 1 lists the temperature at which the maximum conversion of NO to N₂ was obtained, the total NO_x-conversion at this temperature, and the formation of N₂ and N₂O, respectively, at this temperature. It should
25 be noted that conversion into N₂ is desired in this case, while conversion into N₂O is undesired.

Table 1

SAMPLE	T (°C) max. N ₂ conv.	% NO _x conv.	% formation	
			N ₂	N ₂ O
1 wt% Pt-CHA 30%	280	44	32	12
5 wt% Ag-MOR 70%				
1.5 wt% Pt-MOR 30%	220	100	19	81
5 wt% Ag-CHA 70%				
1 wt% Pt-MOR 100%	200	100	29	71
1 wt% Pt-CHA 100%	260	16	3	9
5 wt% Ag-CHA 100%	500	37	35	2

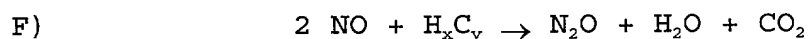
The results in Table 1 indicate that the highest total NO_x-conversion will be achieved with porous samples comprising zeolites of Pt-Mordenite type. However, the strong formation of dinitrogen oxide (N₂O) with Pt-Mordenite is a draw-back. The combined Pt-CHA/Ag-MOR sample exhibited very high conversion of NO_x into N₂. Also the Ag-CHA sample exhibited a high conversions of NO₂ to N₂ but only at a very high temperature (500 °C), which is impractical for many applications.

In Table 2 below, the catalytic conversion efficiency from further evaluations of different zeolites, and physical mixtures of same, are listed. The catalytic conversion efficiency is listed both for the case when the hydrocarbon (C₈H₁₈) in the supplied gas mixture is a linear alkane, i.e. n-octane, and for the case when the hydrocarbon (C₈H₁₈) is a strongly branched iso-paraffin, i.e. iso-octane (more specifically 2,2,4-trimethylpentane).

Table 2

SAMPLE	T(°C) max. N ₂ conv.	% NO _x conv.		% formation			
		n-	iso-	N ₂ n-	N ₂ O iso-	n-	iso-
0.5 wt% Pt-FER 30%							
5 wt% Ag-FER 70%	280	32	19	8	4	24	15
1.5 wt% Pt-MOR 20%							
5 wt% Ag-FER 80%	260	30	32	4	8	26	24
0.5 wt% Pt-FER 30%							
5 wt% Ag-MOR 70%	260	56	86	23	58	33	28
0.5 wt% Pt-FER 100%	240	62	16	15	9	47	7
5 wt% Ag-MOR 100%	360	15	15	13	13	2	2

As is evident from Table 2, the sample comprising Pt-Ferrierite alone (Pt-FER) provided a very high total NO_x-conversion when the supplied hydrocarbon is a linear hydrocarbon, i.e. n-octane. This is a result from reaction of the linear hydrocarbon over the Pt-catalyst, according to the earlier mentioned reaction F):



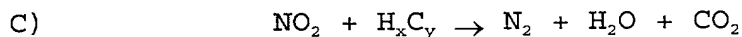
As a result of this reaction, the formation of undesired dinitrogen oxide N₂O is very high when supplying the linear hydrocarbon.

When instead the strongly branched iso-octane was supplied to the Pt-FER sample, the total NO_x-conversion dropped drastically. The reason for this is that the strongly branched iso-octane is sterically prevented from coming into contact with the Pt-catalyst, because of the rather small entrances into the internal pore structure of the Pt-Ferrierite, inside of which the main portion of the Pt-

catalyst is located. The linear hydrocarbon, on the other hand, is not sterically prevented from coming into contact with the Pt-catalyst in the internal pore structure, and therefore reaction F) can take place and consume NO.

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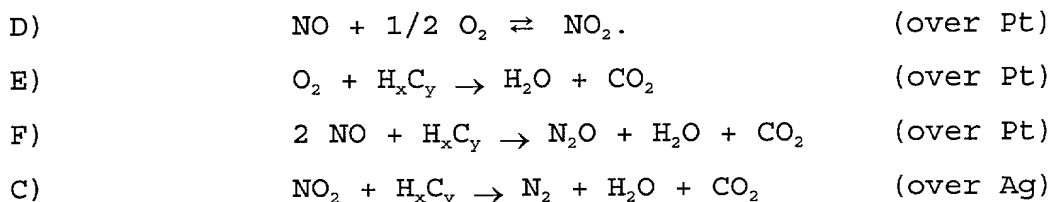
As is also evident from Table 2, the porous sample comprising Ag-Mordenite alone provides a fairly low total NO_x-conversion, and there is no difference in conversion efficiency when supplying n-octane and iso-octane, respectively. This result indicates that the strongly branched iso-octane is not sterically prevented from coming into contact with the Ag-catalyst to any higher extent than the linear n-octane. The reason for the low total NO_x-conversion in this case is that the amount of nitrogen dioxide (NO₂) in the test gas is too small to allow the earlier mentioned reaction C) to take place over the Ag-catalyst:



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From these results, it can be concluded that Ferrierite-zeolites will admit linear hydrocarbons into their internal pore structure, but will not admit strongly branched hydrocarbons. Furthermore, it can be concluded that Mordenite-zeolites will admit both linear and strongly branched hydrocarbons into their internal pore structure.

Accordingly, a mixture of Pt-Ferrierite and Ag-Ferrierite should admit linear hydrocarbons, e.g. n-octane, and allow the four following reactions to take place over the combined Pt/Ag-catalyst sample:

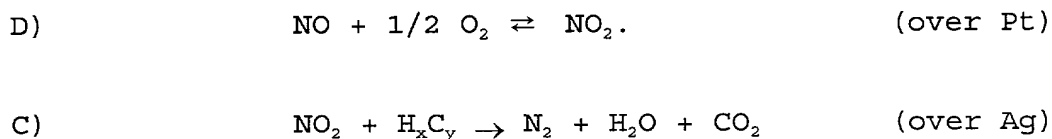


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When the branched iso-octane is supplied instead, there will be less reaction according to reactions E), F) and C), since the branched iso-octane is at least partially sterically prevented from participating. The result of this is that the total NO_x -conversion drops, when supplying the branched iso-octane, as is evident from Table 2 (Pt-FER/Ag-FER). This is further illustrated by the attached Graphs 1A and 1B.

15 When using a porous material comprising a combination of Pt-Ferrierite and Ag-Mordenite (Pt-FER/Ag-MOR), the linear n-octane will have access into the internal pore structures of both the Pt-Ferrierite and the Ag-Mordenite. Accordingly, all four reactions D, E, F and C can take place. This results in a rather high total NO_x -conversion when supplying linear n-octane, as can be seen from the results in Table 2.

25 As earlier discussed, the branched iso-octane is sterically prevented from getting into the pore structure of a Ferrierite-zeolite, but is not prevented from getting into the pore structure of a Mordenite-zeolite. Accordingly, when a branched hydrocarbon, e.g. iso-octane, is supplied to the physical mixture of Pt-Ferrierite and Ag-Mordenite, the reactions D and C will be predominant:



35

This is indicated in Table 2 (Pt-FER/Ag-MOR) as a surprising increase of the total NO_x-conversion, and a pronounced decrease of the relative N₂O-formation, when the branched iso-octane is supplied instead of the linear
5 n-octane. This effect is very useful for improving the catalytic conversion efficiency, and is further illustrated in the attached Graphs 2A and 2B.

Consequently, according to the present invention, it is an
10 advantage to sterically prevent hydrocarbons, or other reducing agents, from being oxidized according to reactions E) and/or F). A number of further conclusions can be drawn from this fact. This is also the basic principle which the present invention relies upon, as
15 already has become evident from the earlier description.

Although the invention herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative
20 of the principles and applications of the present invention. It is therefore to be understood that numerous modifications may be made to the illustrative embodiments and that other arrangements may be devised without departing from the spirit and scope of the
25 present invention as defined by the appended claims.

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POROUS MATERIAL, METHOD AND ARRANGEMENT FOR CATALYTIC
CONVERSION OF EXHAUST GASES

5 TECHNICAL FIELD:

10 The invention pertains to a porous material for catalytic
conversion of exhaust gases. The porous material comprises
a carrier with a first porous structure, and an oxidation
catalyst which in the presence of oxygen has the ability to
catalyse oxidation of nitrogen monoxide into nitrogen
dioxide. The oxidation catalyst in itself also has the
ability to catalyse oxidation of a reducing agent but,
according to the invention, the oxidation of the reducing
15 agent is prevented by means of the oxidation catalyst being
enclosed inside the first porous structure, which has such
dimensions that the reducing agent is sterically prevented
from coming into contact with the oxidation catalyst.

20 Preferably, the porous material also comprises a carrier
with a second porous structure and a reduction catalyst,
which in the presence of the reducing agent is able to
selectively catalyse reduction of nitrogen dioxide into
nitrogen, whereby the reducing agent is at least partially
25 consumed. The reduction catalyst is thereby located in the
second porous structure which has such dimensions that the
reducing agent can come into contact with the reduction
catalyst. The invention also relates to a method and an
arrangement which utilize the porous material, and
30 indicates an advantageous use of the porous material.

The invention may be applied within the field of catalytic
conversion of exhaust gases which originate from internal
combustion engines, particularly Lean Combustion engines
35 (LC-engines) and diesel engines.

The present invention may also be utilized for other exhaust gases, containing nitrogen oxides and having an oxygen surplus, which originate from stationary emission sources such as gas turbines, power plants and the like.

5

BACKGROUND OF THE INVENTION:

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When attempting to reduce the emissions of nitrogen oxides (NO_x) from internal combustion engines, a lot of efforts have been made to modify the combustion conditions in order to reduce the NO_x -emissions, while still maintaining the combustion efficiency at a satisfactory level.

15

20

Amongst the traditional techniques for the reduction of NO_x -emissions may, inter alia, the technique of Exhaust Gas Recirculation (EGR) be mentioned, as well as special designs of fuel injectors and combustion chambers. Other important parameters are compression, fuel injection time and fuel injection pressure. Techniques involving water injection, the use of fuel/water emulsions and so-called Selective Catalytic Reduction (SCR) by ammonia, have also been employed. Thereby, it has been found that a one-sided optimization of the combustion efficiency often results in increased NO_x -emissions.

25

30

Today, it is required that both the fuel consumption and the NO_x -emissions are reduced. There are also strong demands on reduced emissions of other chemical compounds which are potentially hazardous to the environment, e.g. hydrocarbons.

35

Accordingly, there is an increased need for catalytic converters which also are able to treat exhaust gases from so-called Lean Combustion (LC) engines. Therefore, a number of different catalytic converters have been developed and

are well-known from commercial applications in e.g. motor vehicles.

Typically, conventional catalytic converters comprise one or several matrices, or monolith bricks as they sometimes are called. Such bricks or monoliths are in the form of a ceramic honeycomb substrate, with through passages or cells, and can be furnished with a porous surface coating. Particles of a suitable catalyst are embedded in the surface of the matrix, and the design of the matrix has been optimized in order to maximise the surface area over which catalytic reactions take place. Common catalysts are noble metals, e.g. silver (Ag), platinum (Pt), palladium (Pd), rhodium (Rh), gallium (Ga) or ruthenium (Ru) or mixtures of these. There are also a number of other metals and metal oxides which may be used as catalysts. Such catalysts may have the ability to catalyse oxidation or reduction reactions, or both.

It is also previously known to use crystalline aluminium silicates, so-called zeolites, loaded with a suitable catalyst. The use of zeolites in connection with the catalytic conversion of exhaust gases is disclosed in e.g. EP 0 499 931 A1 and EP 0 445 408 A.

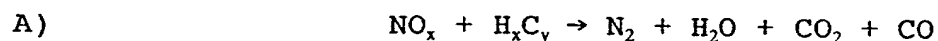
Furthermore, it is also previously known to combine several different catalytic matrices, or to arrange a so-called after-burner in the catalytic conversion process. Such arrangements are disclosed in e.g. U.S. Patent No. 5,465,574.

It is also previously known to use a honeycomb monolith of corrugated metal foil, having a suitable catalyst carried or supported on its surface.

It has also been suggested, e.g. in EP 0 483 708 A1, to combine a conventional ceramic catalytic converter with an electrically heatable catalytic converter in order to ensure that the optimum temperature for catalytic conversion is maintained.

Thus, a number of different catalyst materials, devices, and arrangements for the catalytic conversion of exhaust gases have been described in the art.

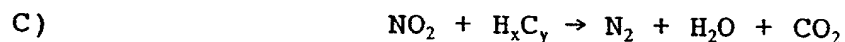
Thereby, it is believed that simultaneous elimination of nitrogen oxides (NO_x) and hydrocarbons (H_xC_y) may take place over e.g. an Ag-catalyst, according to the (simplified) chemical reactions:



and



However, in practice, it has been found that the following reaction is predominant:



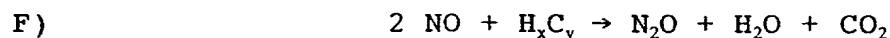
It should be noted that the term H_xC_y in the chemical reactions herein not only refers to hydrocarbons but is also relevant for other reducing agents which further comprise oxygen and/or sulphur. Accordingly, the reducing agent H_xC_y could also be expressed as $\text{H}_x\text{C}_y\text{O}_z\text{S}_w$. Examples of reducing agents which might be present in exhaust gases are alkanes, alkenes, paraffines, alcohols, aldehydes, ketones, ethers or esters and different sulphur-containing compounds. Also CO or H_2 could act as reducing agents. The reducing agent in the exhaust gases can originate from the

fuel or the combustion air, or it can be added to the exhaust gases on purpose.

It has earlier been found that the above-mentioned reaction according to C) is very rapid over e.g. Ag-catalysts. Acidic catalysts (H^+) and acidic zeolites, doped with Ag or other suitable catalysts, have been found to be selective in the sense that NO_2 will readily be converted, whereas NO will not. This can be a great disadvantage since NO is predominant in "lean" exhaust gases from e.g. LC-engines. Another problem is that the available amount of NO_2 can become limiting for the reduction of hydrocarbons (H_xC_y) or other undesired compounds.

In order to solve this problem, i.e. to be able to reduce the amount of both NO and H_xC_y in the exhaust gases, it has earlier been suggested to combine an Ag-zeolite catalyst with a Pt-catalyst.

Normally, the following main reactions will take place over a conventional Pt-catalyst:



When using a conventional Ag-zeolite catalyst in combination with a conventional Pt-catalyst, all four reactions C), D), E) and F) will occur. However, since hydrocarbon (H_xC_y) is consumed in the chemical reactions E) and F), there is a risk that there will not be a sufficient amount of hydrocarbon (H_xC_y) left for the reaction with nitrogen dioxide (NO_2), according to reaction C). This results in an undesired residue of nitrogen dioxide (NO_2)

in the catalytically converted exhaust gases, originating from reaction D).

Previous attempts have been made to solve this problem with different types of catalysts, by means of combining different catalysts, and by means of adding an additional amount of hydrocarbon to the exhaust gases in order to supply the reaction C) with a sufficient amount of hydrocarbon.

However, many of the previous solutions have been associated with the problem of undesired oxidation of hydrocarbons (H_xC_y) over at least some surfaces of the oxidation catalyst, which preferably only should catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), according to reaction D).

Another problem associated with many previously known catalysts is that, during certain conditions, they will catalyse reaction F) which produces dinitrogen oxide (N_2O). This reaction is undesired and it is preferred that the nitrogen oxides (NO_x) in the exhaust gases are converted into nitrogen (N_2) to the highest possible degree, and not into dinitrogen oxide (N_2O).

TECHNICAL PROBLEM:

Accordingly, there is a need for a new, selective oxidation catalyst material, which catalyses oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and which does not catalyse oxidation of hydrocarbons.

Furthermore, there is also a need for an effective combination of such a selective oxidation catalyst material, catalysing a reaction which produces nitrogen dioxide (NO_2), and a reduction catalyst material,

catalysing a reaction in which nitrogen dioxide (NO_2) is reduced by hydrocarbons or other reducing agents into nitrogen (N_2).

5 SUMMARY OF THE INVENTION:

Accordingly, a first object of the present invention is to provide a porous material for catalytic conversion of exhaust gases, by means of which porous material it is possible to selectively catalyse the oxidation of nitrogen
10 monoxide (NO) into nitrogen dioxide (NO_2), and avoid catalytic oxidation of hydrocarbons (H_xC_y) or other reducing agents.

15 This first object of the invention is achieved by means of a porous material for catalytic conversion of exhaust gases which, according to claim 1, comprises a carrier with a first porous structure, and an oxidation catalyst. In the presence of oxygen, the oxidation catalyst has the ability
20 to catalyse oxidation of nitrogen monoxide into nitrogen dioxide, according to a first reaction. Furthermore, the oxidation catalyst in itself has the ability to catalyse oxidation of a reducing agent, according to a second reaction. According to the invention, the oxidation
25 catalyst is enclosed inside the porous structure, which has such dimensions that the reducing agent is sterically prevented from coming into contact with the oxidation catalyst. This will enable primarily the first reaction, out of said first and second reactions, to take place over
30 the oxidation catalyst during the catalytic conversion of the exhaust gases.

Furthermore, a second object of the present invention is to provide a porous material for catalytic conversion of
35 exhaust gases, wherein primarily only the desired reactions take place, as a result of which the contents of NO , NO_2

and H_xC_y in the catalytically converted exhaust gases are effectively decreased, and the resulting conversion products primarily are N_2 , CO_2 and H_2O , and not N_2O .

5 The second object of the invention is achieved by means of a porous material according to claim 1 which, in accordance with claim 2, further comprises a carrier with a second porous structure and a reduction catalyst. In the presence of a reducing agent, the reduction catalyst is able to
10 selectively catalyse reduction of nitrogen dioxide into nitrogen, according to a third reaction, whereby the reducing agent participates in the third reaction and is at least partially consumed. Thereby, the reduction catalyst is located in the second porous structure, which has such
15 dimensions that the reducing agent can come into contact with the reduction catalyst in order to enable the third reaction to take place.

20 A third object of the present invention is to provide a method for catalytic conversion of exhaust gases in which the porous material according to the invention is utilized.

25 The third object of the invention is achieved by means of a method for catalytic conversion of exhaust gases which, according to claim 23, comprises oxidation of nitrogen monoxide into nitrogen dioxide over an oxidation catalyst, according to a first reaction, whereby said oxidation catalyst also has the ability to, according to a second
30 reaction, catalyse oxidation of a reducing agent. According to the invention, however, the reducing agent is sterically prevented from coming into contact with the oxidation catalyst, as a result of which primarily the first reaction, out of said first and second reactions, takes place over the oxidation catalyst.
35

A fourth object of the present invention is to indicate an advantageous use of the porous material according to the invention.

5 In accordance with the invention, the fourth object is achieved by the use of a porous material according to the invention, providing functions both for the oxidation of nitrogen monoxide into nitrogen dioxide and for the reduction of nitrogen dioxide into nitrogen, for catalytic
10 conversion of exhaust gases which have an oxygen surplus.

Finally, a fifth object of the present invention is to provide an advantageous arrangement for catalytic conversion of exhaust gases, utilizing the porous material
15 according to the invention.

In accordance with the invention, the fifth object of the invention is achieved by an arrangement, for catalytic conversion of exhaust gases from an internal combustion
20 engine, comprising a porous material according to the invention.

BRIEF DESCRIPTION OF THE DRAWINGS:

25 In the following, the invention will be described in greater detail with reference to the attached drawings and graphs.

Fig. 1 shows a schematic view of a portion of a porous
30 material according to the invention, also with an enlarged view seen from inside a pore in the porous material. The major chemical reactions which occur during the catalytic conversion of exhaust gases are also indicated.

Fig. 2 schematically depicts an embodiment of the porous material according to the invention, with an enlarged detailed view of a portion of the porous material including a supporting substrate.

Fig. 3A schematically shows an enlarged detailed view of a portion of the enlarged detailed view in Fig. 2, and depicts a variant of the porous material according to the invention, comprising a physical mixture of two different zeolite carriers.

Fig. 3B schematically shows another enlarged detailed view of a portion of the enlarged detailed view in Fig. 2, and depicts another variant of the porous material according to the invention, comprising a layered structure of two different zeolite carriers.

Fig. 3C schematically shows an alternative to the layered structure in Fig. 3B.

Fig. 4A schematically shows an embodiment of a porous material according to the invention, having a first portion and a second portion.

Fig. 4B schematically shows another embodiment of the invention, wherein the porous material according to the invention comprises two separate, different parts, intended to be used together in a single catalytic conversion process.

Fig. 5 shows a schematic process diagram of an arrangement for catalytic conversion of exhaust gases according to the invention.

Graph 1A shows results from a laboratory evaluation of a porous sample, comprising a physical mixture of Pt-Ferrierite and Ag-Ferrierite, when a linear hydrocarbon is supplied in the gas which is to be catalytically converted.

Graph 1B shows results from a laboratory evaluation of the same porous sample as in Graph 1A, but when a branched hydrocarbon is supplied in the gas which is to be catalytically converted.

Graph 2A shows results from a laboratory evaluation of a porous material according to the invention, comprising a physical mixture of Pt-Ferrierite and Ag-Mordenite, when a linear hydrocarbon is supplied in the gas which is to be catalytically converted.

Graph 2B shows results from a laboratory evaluation of the same porous material according to the invention as in Graph 2A, but when a branched hydrocarbon is supplied in the gas which is to be catalytically converted.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS:

In the following, a porous material according to the invention will be described with reference to the attached drawings.

The porous material 1 in Fig. 1 comprises a carrier with a first porous structure 2, 2'. An oxidation catalyst (OX) is enclosed inside the first porous structure 2, 2'. In the presence of oxygen (O_2), the oxidation catalyst (OX) has the ability to catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2), according to a first reaction

3. Furthermore, the oxidation catalyst (OX) in itself has the ability to catalyse oxidation of a reducing agent (HC), according to a second reaction (not present in Fig. 1).

5 According to the invention, however, such oxidation of the reducing agent according to the second reaction is not desired, since the reducing agent (HC) is more useful in a third reaction, as will become apparent below.

10 In order to prevent the undesired second reaction from occurring, the oxidation catalyst (OX) is enclosed inside the first porous structure 2, 2', which has such dimensions that the reducing agent (HC) is sterically prevented 4, 4' from coming into contact with the oxidation catalyst (OX).
15 This will enable primarily the desired first reaction 3, out of said first and second reactions, to take place over the oxidation catalyst (OX) during the catalytic conversion of exhaust gases. In this context, the term "first porous structure" primarily refers to internal micro-pores in the carrier material or micro-pores between carrier particles
20 or grains.

Preferably, the porous material 1 further comprises a carrier with a second porous structure 5, 5', in which a
25 reduction catalyst (RED) is located. In this context, the term "second porous structure" can include internal micro-pores in the carrier material, or cavities or channels between carrier particles, but also cavities inside or channels through the porous material, i.e. macro-pores. In
30 the presence of a reducing agent (HC), the reduction catalyst (RED) is able to selectively catalyse reduction of nitrogen dioxide (NO_2) into nitrogen (N_2), according to a third reaction 6, shown schematically i Fig. 1. Thereby, the reducing agent (HC) participates in the third reaction
35 6 and is at least partially consumed.

According to the invention, the reduction catalyst (RED) is located in the second porous structure 5, 5', which has such dimensions that the reducing agent (HC) can come into contact with the reduction catalyst (RED). This enables the desired third reaction 6 to take place during the catalytic conversion of exhaust gases.

According to one embodiment of the porous material according to the invention, the first porous structure 2, 2' on an average exhibits smaller entrances 7 for the reducing agent (HC) than the second porous structure 5, 5'. In this way, the reducing agent (HC) is prevented from getting into contact with the oxidation catalyst (OX), enclosed inside the first porous structure 2, 2', but is not prevented from coming into contact with the reduction catalyst (RED) in the second porous structure 5, 5'. The pores in the first porous structure 2, 2' should preferably primarily have an effective size of 3-6 Å.

According to another embodiment of the porous material, both the first 2, 2' and the second 5, 5' porous structures are provided in the same layer or coating of the porous material.

If desired, however, the first 2, 2' and the second 5, 5' porous structures can be provided in different layers/coatings of the porous material. This might be an advantage, depending on the composition of the exhaust gases which are to be catalytically converted.

In one embodiment of the porous material, the carrier with the second porous structure 5, 5' is adapted to the molecule size and/or the adsorption properties of the reducing agent (HC) or agents, which is/are expected to occur in the exhaust gases.

In another embodiment of the porous material, the ratio between the oxidation catalyst (OX) and the reduction catalyst (RED) has been optimized so that the production of nitrogen dioxide (NO_2), according to the first reaction 3, essentially corresponds to the consumption of nitrogen dioxide (NO_2), according to the third reaction 6.

In still another embodiment of the invention (Fig. 4A), the porous material further comprises a first portion 10 and a second portion 11, wherein the first portion 10 is intended to receive exhaust gases 12 before the second portion 11 during the catalytic conversion. Thereby, the first portion 10 contains a larger quantity of the oxidation catalyst (OX) than the second portion 11, whereas the second portion 11 contains a larger quantity of the reduction catalyst (RED) than the first portion 10. Accordingly, in a flow of exhaust gases the first reaction 3, producing NO_2 , will take place upstream the third reaction 6, which consumes NO_2 . As shown in Fig. 4B, it is also conceivable with embodiments wherein the first and second portions are separated from each other, as long as they are used for catalytic conversion in the same conversion process.

According to one embodiment of the porous material, the first 2, 2' and/or the second 5, 5' porous structure is provided in a carrier which is a zeolite crystal structure.

Furthermore, both the first 2, 2' and the second 5, 5' porous structures can be provided in carriers of zeolite type, wherein preferably the first porous structure 2, 2' is provided in a first zeolite 14 and the second porous structure in a second zeolite 15.

As earlier mentioned, according to the invention, the first porous structure 2, 2' and, accordingly, also the first zeolite 14 should provide suitable properties in order to

prevent the earlier-mentioned, undesired second reaction from taking place.

There are a number of different ways of combining different zeolites in a porous material according to the invention. Accordingly, the porous material can comprise a physical mixture 13 of the first zeolite 14 and the second zeolite 15 (Fig. 3A).

Furthermore, the porous material can comprise a layered structure 16, 17 of the first zeolite and the second zeolite (Figs. 3B and 3C). Different layers may also be applied or coated onto different supporting substrates 18 or different surfaces of a substrate 18.

In certain applications, it may be preferred to arrange the layered structure 17 so that, in a flow of exhaust gases, the second zeolite will encounter the exhaust gases before the first zeolite. This might be the case e.g. when the exhaust gases which are to be converted contain a proportionately high content of NO₂ but a low content of NO.

In other applications, e.g. when the content of NO in the exhaust gases is proportionately high but the content of NO₂ is low, it might be desirable to arrange the layered structure 16 in the opposite way, i.e. the first zeolite outside the second zeolite.

According to one embodiment of the porous material, a layered structure is achieved by means of the second zeolite 15, which provides the second porous structure 5, 5', being crystallized onto the first zeolite 14, which provides the first porous structure 2, 2'. This can be done by means of so-called over-growth.

Another embodiment of the porous material aims at further reducing the occurrence of the earlier-mentioned, undesired second reaction. In this embodiment, the content of oxidation catalyst (OX) has been reduced in the outer layers 8 of the first zeolite by means of partial ion-exchange (indicated in Fig. 1). Methods for altering the penetration depth and dispersion of the catalytically active metals are well-known to the skilled person and will not be described in any greater detail.

In another embodiment of the porous material, an additional zeolite crystal layer with a reduced content of oxidation catalyst (OX) has been crystallized onto the first zeolite, by means of so-called over-growth. Thereby, the additional layer advantageously comprises a zeolite which provides a porous structure with even smaller pores/entrances than the first zeolite. In this way, undesired reducing agent can more effectively be prevented from getting inside the internal pore structure of the first zeolite, at the same time as the nitrogen oxide (NO) will be admitted and can move freely inside said internal pore structure.

Also the dimensions of the crystal grains in the zeolite crystal structures can be used in order to facilitate desired chemical reactions, and in order to prevent undesired chemical reactions. Different crystal structures can be achieved in several different ways, e.g. by means of the choice of the crystallization conditions and the choice of zeolite type. Also the internal pore structure of the zeolites is influenced by the choice of zeolite type.

Thus, according to one embodiment of the porous material, the size and shape of the crystal grains in the crystal structure of the first zeolite, has been optimized both in order to prevent access for the reducing agent (HC), and in order to allow oxidation of NO to NO₂. The optimization of

the grain size is important since it makes it possible to maximise the oxidation of NO into NO₂, and to minimize the oxidation of HC.

5 In another embodiment of the porous material, a proportionately small pore size, in the crystal structure of the first zeolite which provides the first porous structure 2, 2', has been achieved by means of selecting a Ferrierite-zeolite or a Chabazite-zeolite, and not e.g. a
10 Mordenite-zeolite.

As earlier mentioned, the porous material according to the invention has the ability to catalyse oxidization of nitrogen monoxide (NO) into nitrogen dioxide (NO₂), and preferably also the ability to selectively catalyse
15 reduction of nitrogen dioxide (NO₂) into nitrogen (N₂) in the presence of a reducing agent (HC). Thereby, the reducing agent (HC) may be any suitable reducing agent which is present in, or added to, the exhaust gases which
20 are to be catalytically converted.

It is an advantage, however, if the reducing agent (HC) in the exhaust gases is a hydrocarbon (H_xC_y) or a chemical compound comprising oxygen and sulphur (H_xC_yO_zS_w). These
25 compounds can originate from the fuel which is combusted and will, as earlier mentioned, be at least partially consumed according to the earlier-mentioned third reaction 6 over the reduction catalyst (RED). Alternative fuels, e.g. rape methyl ether, may produce oxygen-containing
30 compounds, whereas sulphur is frequently present in most fuels.

The reduction catalyst (RED) in the second porous structure 5, 5' might be of any suitable, previously known type.
35 However, in the porous material according to the invention, the reduction catalyst (RED) preferably comprises Brönstedt

acid sites, and silver (Ag), copper (Cu) or Rhodium (Rh), Cobalt (Co), Indium (In), Iridium (Ir) or combinations of these. In the porous material according to the invention, acidic zeolite catalysts are preferred as reduction catalysts (RED) .

The oxidation catalyst (OX) may be of any type suitable for the purpose, but preferably comprises platinum (Pt) and/or Palladium (Pd).

The herein used term "porous material" should be regarded as including the entire structure/mass which might be present inside a unit for the catalytic conversion of exhaust gases. Accordingly, the term "porous" should be understood both in a microscopic and in a macroscopic sense, i.e. the porous material could comprise elements which in themselves are not porous to exhaust gases. However, the material structure as a whole, i.e. the "porous material" according to the invention, will allow the exhaust gases which are to be catalytically converted to pass through. It should also be noted that embodiments wherein the porous material is composed of several separated parts, having different structures and functions, are conceivable, as long as they are used in the same catalytic conversion process.

The porous material, according to the invention, may be coated onto one or several suitable substrates or matrixes in order to provide a carrier or several carriers which comprise the first or/and the second porous structures. Suitable substrates for this purpose are well-known from the prior art, and will not be described in any greater detail especially since they are of minor importance for the invention.

Accordingly, the substrate 18 may be a metal substrate of a previously known type. The substrate 18 may also be a supporting, previously known, honeycomb structure of a suitable material, with or without catalytic activity.

5

It should also be noted that the term "porous structure" used herein should be understood as to include both micro-pores and macro-pores of the porous material. Accordingly, internal micro-pores, cavities between carrier particles, channels inside or through the porous material, etc., are all included within the scope of "porous structure".

10

For instance, there is no need for the second porous structure 5, 5' to be an internal micro-pore structure inside a carrier material, but the second porous structure 5, 5' could instead be provided by a more open, macroscopic structure. The first porous structure 2, 2', however, is preferably an internal micro-structure inside a carrier material, in order to provide sufficient sterical hindrance against the admittance of the (undesired) reducing agent into the sites where the oxidation catalyst is situated.

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In the following, a method for catalytic conversion of exhaust gases, according to the invention, will be described in greater detail with reference to the attached Figs. 1 and 5. The method according to the invention comprises oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO₂) over an oxidation catalyst (OX), according to a first reaction 3 (Fig. 1). The oxidation catalyst (OX) in itself has the ability to catalyse oxidation of a reducing agent (HC), according to a second reaction (not present in Fig. 1). According to the invention, however, the reducing agent (HC) is sterically prevented 4, 4' from coming into contact with the oxidation catalyst (OX). As a result of this, primarily the first reaction 3, out of said first and

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second reactions, takes place over the oxidation catalyst (OX).

According to one embodiment of the invention, the method further comprises reduction of nitrogen dioxide (NO_2) into nitrogen (N_2) over a reduction catalyst (RED) in the presence of a reducing agent (HC), according to a third reaction 6. Thereby, the reducing agent (HC) participates in the third reaction 6 and is at least partially consumed. In this way, catalytically converted exhaust gases 12' (Fig. 5), having a reduced content of nitrogen monoxide (NO), nitrogen dioxide (NO_2) and reducing agent (HC) and a proportionately low content of dinitrogen oxide (N_2O), are obtained. Furthermore, the converted exhaust gases will have a reduced content of carbon monoxide (CO).

When desirable, an additional amount 19, 19', 19'' of reducing agent (HC) can be added with a suitable injection device 28, before reduction takes place over the reduction catalyst (RED), according to the third reaction 6 (Figs. 1 and 5). In this way, the stoichiometrics of the occurring chemical reactions can be influenced so that the catalytic conversion becomes as complete as possible. In internal combustion engines, it is also possible to increase or regulate the amount of available reducing agent by means of so-called engine parameter tuning. This can be done by e.g. fuel injection timing, valve timing, post-injection, control of charging pressure and/or fuel injection pressure, EGR, transmission ratio, etc.

Advantageously, the additional amount 19, 19', 19'' of reducing agent (HC) can be regulated on the basis of a measured or previously mapped content 20 of reducing agent (HC) and/or nitrogen oxides (NO_x) in the exhaust gases 12, 12'.

The measured content 20 of reducing agent (HC) or nitrogen oxides (NO_x) in the catalytically converted exhaust gases (12') can also be used in a diagnostic control system 22, providing an indication of the status of the catalytic conversion.

The exhaust gases 12 can also be passed through a device having the ability to store and when necessary release nitrogen oxides (NO_x) before the oxidation over the oxidation catalyst (OX), according to the first reaction 3. Such NO_x -absorbers are well-known to the person skilled in the art, and will not be described in any greater detail herein. Before the oxidation, the exhaust gases 12 can also be passed through a previously known device having the ability to store, and when necessary release, reducing agent (HC), e.g. hydrocarbon. This embodiment is useful for e.g. cold starts of an internal combustion engine.

In order to ensure that the oxidation catalyst (OX) and/or the reduction catalyst (RED) is functioning in the best possible way, i.e. are within an active temperature interval, the temperature of the exhaust gases can be regulated before the passage through the porous material 21 according to the invention. This can be done with any previously known device 23 which is suitable for the purpose.

In order to further improve the catalytic conversion, the exhaust gases can be allowed to pass a second oxidation catalyst 24, over which oxidation of residues of reducing agent and/or carbon monoxide can take place. In this way, it is ensured that the exhaust gases, which have been at least partially catalytically converted over the porous material 21, reach a sufficiently high degree of catalytic conversion.

It is advantageous for the method of the invention if the exhaust gases 12 originate from an internal combustion engine 25, and the reducing agent (HC) comprises a hydrocarbon (H_xC_y) and/or a chemical compound ($H_xC_yO_zS_w$) further comprising oxygen and/or sulphur.

Furthermore, the fuel 26 consumption of the internal combustion engine 25 will influence the chemical composition of the exhaust gases 12. Legislative regulations are imposed both on fuel consumption and the residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases 12'. In one embodiment of the invention, both the fuel consumption of the internal combustion engine, and the residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases 12', are regulated in order to fulfil the relevant legislative regulations.

In one preferred embodiment of the method according to the invention, the internal combustion engine 25 is a diesel engine and the reducing agent (HC) originates from internal combustion in said diesel engine.

When diesel engines are concerned, an additional amount of reducing agent (HC) can advantageously be supplied to the engine via a fuel injector of the diesel engine and/or via a separate injector for additional reducing agent.

It is preferred to use a porous material according to the invention, for catalytic conversion of exhaust gases 12, which have an oxygen surplus and, accordingly, are difficult to convert in conventional catalytic converters, e.g. three-way converters. In such use, the porous material provides functions both for the oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and for the reduction of nitrogen dioxide (NO_2) into nitrogen (N_2).

It is also preferred with an arrangement 27, according to the invention, for catalytic conversion of exhaust gases which originate from an internal combustion engine 25. Thereby, the arrangement comprises a porous material 21 according to the invention or, furthermore, operates through a method according to the invention.

EXAMPLE:

In order to more clearly illustrate the basic principles of the present invention, a number of porous samples, i.e. model catalyst materials, were produced in a series of laboratory trials.

In the laboratory trials, zeolites of the basic types Mordenite, Ferrierite and Chabazite were used in order to provide catalyst carriers.

The different zeolite types had the following channel/pore dimensions:

Mordenite: free diameter: 12 rings 6.5 x 7.0 Å
 8 rings 2.6 x 5.7 Å

Ferrierite: free diameter: 10 rings 4.2 x 5.4 Å
 8 rings 3.5 x 4.8 Å

Chabazite: free diameter: 8 rings 3.8 x 3.8 Å

As evident from above, the selected zeolites had either 8 rings, 10 rings or 12 rings, providing entrances into their internal micro-pore structure. The selected zeolite raw materials were provided in the form of NH₄-zeolites.

Preparation of platinum-zeolites (Pt)

Samples of the different NH_4 -zeolites were calcined during 1 h at 500 °C under oxygen flow in order to transfer the zeolites into acidic form, i.e into H-zeolites. Amounts of 0.5 wt-%, 1.0 wt-% or 1.5 wt-% of platinum (PT) were loaded onto the H-zeolites by means of contacting them with an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$. Thereby, the 0.01 M Pt-solution was added dropwisely to zeolite dispersed in water. The obtained mixtures were stirred during 24 h at room temperature, filtered, washed with H_2O , and dried overnight at 60 °C. Thereafter, the samples were calcined during 2 h at 450 °C in dry air, with a rate of 0.5 °C x min^{-1} , whereafter the samples were cooled down in a N_2 -flow.

Methods for Pt-loading are described in greater detail in the publications J. Catal. 113 (1988), p. 220-235 (Tzou et al.) and J. Catal. 117 (1989), p. 91-101 (Homeyer et al.).

Preparation of silver-zeolite (Ag)

Ag-zeolites were produced by loading 5 wt-% Ag onto the different NH_4 -zeolites by means of impregnation with AgNO_3 , using the so-called "incipient wetness" method. Thereby, the metal salt (AgNO_3) was dissolved in a minimum of water (1 ml/gram of zeolite), whereafter the obtained solution was mixed with the zeolite powders. Finally, the samples were calcined during 16 h at 550 °C in a muffle furnace and stored in the dark until evaluation took place.

Evaluation of catalytic conversion efficiency

Before the evaluation, the obtained Pt-zeolites and Ag-zeolites, and physical mixtures of these, were compressed into pellets, i.e. model porous samples, and the catalytic

conversion efficiency of the different porous samples was evaluated.

In the prepared porous samples, the Pt-zeolites were intended to provide the earlier-mentioned NO-oxidation function, whereas the Ag-zeolites were intended to provide the earlier-mentioned NO₂-reduction function.

The evaluation of the catalytic conversion efficiency was performed by means of inserting a small amount (0.3 ml) of porous sample, into a device suitable for the purpose of evaluating catalytic conversion efficiency. Thereafter, a gas flow of 300 ml/min, with the composition 500 ppm NO, 350 ppm C₈H₁₈, 6% O₂, 12% H₂O, 10% CO₂ and 350 ppm CO, was passed through the sample chamber in which the porous material sample was placed. The temperature was step-wisely increased from 140 till 500 °C, while the composition of the catalytically converted exhaust gases from the sample chamber was detected.

The catalytic conversion efficiency for some of the different porous samples, comprising the different zeolites and physical mixtures of these, is evident from Table 1 below. Table 1 lists the temperature at which the maximum conversion of NO to N₂ was obtained, the total NO_x-conversion at this temperature, and the formation of N₂ and N₂O, respectively, at this temperature. It should be noted that conversion into N₂ is desired in this case, while conversion into N₂O is undesired.

Table 1

SAMPLE	T (°C)max. N ₂ conv.	% NO _x conv.	% formation	
			N ₂	N ₂ O
1 wt% Pt-CHA 30%	280	44	32	12
5 wt% Ag-MOR 70%				
1.5 wt% Pt-MOR 30%	220	100	19	81
5 wt% Ag-CHA 70%				
1 wt% Pt-MOR 100%	200	100	29	71
1 wt% Pt-CHA 100%	260	16	3	9
5 wt% Ag-CHA 100%	500	37	35	2

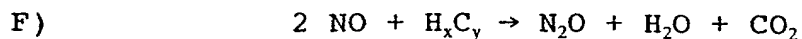
The results in Table 1 indicate that the highest total NO_x-conversion will be achieved with porous samples comprising zeolites of Pt-Mordenite type. However, the strong formation of dinitrogen oxide (N₂O) with Pt-Mordenite is a draw-back. The combined Pt-CHA/Ag-MOR sample exhibited very high conversion of NO_x into N₂. Also the Ag-CHA sample exhibited a high conversions of NO₂ to N₂ but only at a very high temperature (500 °C), which is impractical for many applications.

In Table 2 below, the catalytic conversion efficiency from further evaluations of different zeolites, and physical mixtures of these, are listed. The catalytic conversion efficiency is listed both for the case when the hydrocarbon (C₈H₁₈) in the supplied gas mixture is a linear alkane, i.e. n-octane, and for the case when the hydrocarbon (C₈H₁₈) is a strongly branched iso-paraffine, i.e. iso-octane (more specifically 2,2,4-tri-methylpentane).

Table 2

SAMPLE	T(°C) max. N ₂ conv.	% NO _x conv.		% formation			
		n-	iso-	N ₂		N ₂ O	
				C ₈ H ₁₈	C ₈ H ₁₈	n-	iso-
0.5 wt% Pt-FER 30%							
5 wt% Ag-FER 70%	280	32	19	8	4	24	15
1.5 wt% Pt-MOR 20%							
5 wt% Ag-FER 80%	260	30	32	4	8	26	24
0.5 wt% Pt-FER 30%							
5 wt% Ag-MOR 70%	260	56	86	23	58	33	28
0.5 wt% Pt-FER 100%	240	62	16	15	9	47	7
5 wt% Ag-MOR 100%	360	15	15	13	13	2	2

As is evident from Table 2, the sample comprising Pt-Ferrierite alone (Pt-FER) provided a very high total NO_x-conversion when the supplied hydrocarbon is a linear hydrocarbon, i.e. n-octane. This is a result from reaction of the linear hydrocarbon over the Pt-catalyst, according to the earlier mentioned reaction F):

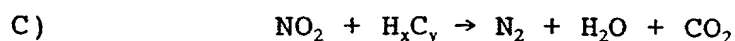


As a result of this reaction, the formation of undesired dinitrogen oxide N₂O is very high when supplying the linear hydrocarbon.

When instead the strongly branched iso-octane was supplied to the Pt-FER sample, the total NO_x-conversion dropped drastically. The reason for this is that the strongly

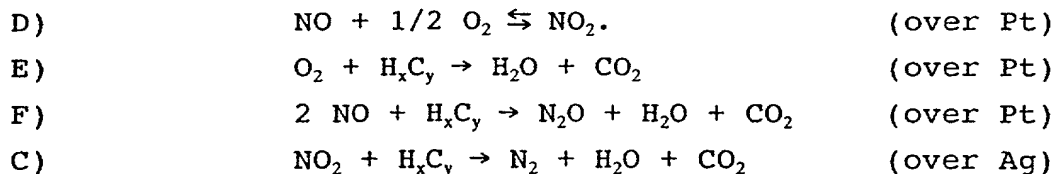
branched iso-octane is sterically prevented from coming into contact with the Pt-catalyst, because of the rather small entrances into the internal pore structure of the Pt-Ferrierite, inside of which the main portion of the Pt-catalyst is located. The linear hydrocarbon, on the other hand, is not sterically prevented from coming into contact with the Pt-catalyst in the internal pore structure, and therefore reaction F) can take place and consume NO.

As is also evident from Table 2, the porous sample comprising Ag-Mordenite alone provides a fairly low total NO_x-conversion, and there is no difference in conversion efficiency when supplying n-octane and iso-octane, respectively. This result indicates that the strongly branched iso-octane is not sterically prevented from coming into contact with the Ag-catalyst to any higher extent than the linear n-octane. The reason for the low total NO_x-conversion in this case is that the amount of nitrogen dioxide (NO₂) in the test gas is too small to allow the earlier mentioned reaction C) to take place over the Ag-catalyst:



From these results, it can be concluded that Ferrierite-zeolites will admit linear hydrocarbons into their internal pore structure, but will not admit strongly branched hydrocarbons. Furthermore, it can be concluded that Mordenite-zeolites will admit both linear and strongly branched hydrocarbons into their internal pore structure.

Accordingly, a mixture of Pt-Ferrierite and Ag-Ferrierite should admit linear hydrocarbons, e.g. n-octane, and allow the four following reactions to take place over the combined Pt/Ag-catalyst sample:



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When the branched iso-octane is supplied instead, there will be less reaction according to reactions E), F) and C), since the branched iso-octane is at least partially sterically prevented from participating. The result of this is that the total NO_x -conversion drops, when supplying the branched iso-octane, as is evident from Table 2 (Pt-FER/Ag-FER). This is further illustrated by the attached Graphs 1A and 1B.

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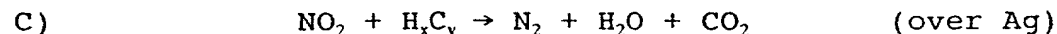
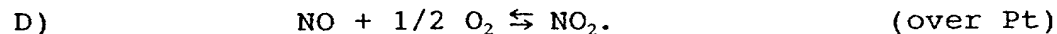
When using a porous material comprising a combination of Pt-Ferrierite and Ag-Mordenite (Pt-FER/Ag-MOR), the linear n-octane will have access into the internal pore structures of both the Pt-Ferrierite and the Ag-Mordenite. Accordingly, all four reactions D, E, F and C can take place. This results in a rather high total NO_x -conversion when supplying linear n-octane, as can be seen from the results in Table 2.

20

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As earlier discussed, the branched iso-octane is sterically prevented from getting into the pore structure of a Ferrierite-zeolite, but is not prevented from getting into the pore structure of a Mordenite-zeolite. Accordingly, when a branched hydrocarbon, e.g. iso-octane, is supplied to the physical mixture of Pt-Ferrierite and Ag-Mordenite, the reactions D and C will be predominant:

30



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This is indicated in Table 2 (Pt-FER/Ag-MOR) as a surprising increase of the total NO_x -conversion, and a pronounced decrease of the relative N_2O -formation, when the branched iso-octane is supplied instead of the linear n-octane. This effect is very useful for improving the catalytic conversion efficiency, and is further illustrated in the attached Graphs 2A and 2B.

Consequently, according to the invention, it is an advantage to sterically prevent hydrocarbons, or other reducing agents, from being oxidized according to reactions E) and/or F). A number of further conclusions can be drawn from this fact. This is also the basic principle which the present invention relies upon, as already has become evident from the earlier description.

The present invention should not be regarded as being limited to the herein described embodiments, but a number of further variants and modifications are conceivable within the scope of the following claims.

5

CLAIMS:

10 1. Porous material for catalytic conversion of exhaust gases, said porous material (1) comprising a carrier with a first porous structure (2, 2'), and an oxidation catalyst (OX) which in the presence of oxygen (O_2), according to a first reaction (3), has the ability to catalyse oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO_2) and, according to a second reaction, to catalyse oxidation of a reducing agent (HC),

15 c h a r a c t e r i z e d i n that the oxidation catalyst (OX) is enclosed inside the first porous structure (2, 2'), which has such dimensions that the reducing agent (HC) is sterically prevented (4, 4') from coming into contact with the oxidation catalyst (OX), in order to enable primarily the first reaction (3), out of said first and second reactions, to take place over the oxidation catalyst (OX) during the catalytic conversion of the exhaust gases.

25

2. Porous material for catalytic conversion of exhaust gases according to claim 1, said porous material (1) further comprising a carrier with a second porous structure (5, 5') and a reduction catalyst (RED), which in the presence of the reducing agent (HC) is able to selectively catalyse reduction of nitrogen dioxide (NO_2) into nitrogen (N_2), according to a third reaction (6), whereby the reducing agent (HC) participates in the third reaction (6) and is at least partially consumed,

30

35 c h a r a c t e r i z e d i n that the reduction catalyst (RED) is located in the second porous structure (5, 5'), which has such dimensions that the reducing agent (HC) can come into contact with the reduction catalyst (RED) in order to enable the third reaction (6) to take place.

3. Porous material for catalytic conversion of exhaust gases according to claim 2,

c h a r a c t e r i z e d i n t h a t t h e f i r s t p o r o u s
structure (2, 2') on an average exhibits smaller entrances
(7) for the reducing agent (HC) than the second porous
structure (5, 5'), and preferably that the first porous
structure primarily comprises pores having an effective
size of 3-6 Å.

4. Porous material for catalytic conversion of exhaust gases according to claim 2 or 3,

c h a r a c t e r i z e d i n t h a t b o t h t h e f i r s t (2, 2')
and the second (5, 5') porous structures are provided in
the same layer/coating of the porous material.

5. Porous material for catalytic conversion of exhaust gases according to claims 2 or 3,

c h a r a c t e r i z e d i n t h a t t h e f i r s t (2, 2') and
the second porous structures (5, 5') are provided in
different layers/coatings of the porous material.

6. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-5,

c h a r a c t e r i z e d i n t h a t t h e c a r r i e r w i t h t h e
second porous structure (5, 5') has been adapted to
molecule size and/or adsorption properties of the reducing
agent (HC).

7. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-6,

c h a r a c t e r i z e d i n t h a t t h e r a t i o b e t w e e n
oxidation catalyst (OX) and reduction catalyst (RED) has
been optimized so that the production of nitrogen dioxide
(NO₂), according to the first reaction (3), essentially
corresponds to the consumption of nitrogen dioxide (NO₂),
according to the third reaction (6).

8. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-7, further comprising a first portion (10) and a second portion (11), wherein the first portion (10) is intended to receive the exhaust gases (12) before the second portion (11) during the catalytic conversion,

characterized in that the first portion (10) contains a larger quantity of the oxidation catalyst (OX) than the second portion (11), whereas the second portion (11) contains a larger quantity of the reduction catalyst (RED) than the first portion (10).

9. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-8,

characterized in that the first (2, 2') and/or the second (5, 5') porous structure is provided in a carrier which is a zeolite crystal structure.

10. Porous material for catalytic conversion of exhaust gases according to claim 9,

characterized in that the porous material comprises a first zeolite (14), providing the first porous structure (2, 2'), and a second zeolite (15), providing the second porous structure (5, 5').

11. Porous material for catalytic conversion of exhaust gases according to claim 10,

characterized in that the porous material comprises a physical mixture (13) of the first zeolite (14) and the second zeolite (15).

12. Porous material for catalytic conversion of exhaust gases according to claim 10,

characterized in that the porous material comprises a layered structure (16, 17) of the first zeolite (14) and the second zeolite (15), wherein said first and

second zeolites (14, 15), depending on the expected composition of the exhaust gases (12) which are to be catalytically converted, have been arranged in relation to each other in said layered structure (16, 17), preferably so that the second zeolite (15) will encounter the exhaust gases (12) before the first zeolite (14) during the catalytic conversion.

13. Porous material for catalytic conversion of exhaust gases according to claim 10,

characterized in that the second zeolite, providing the second porous structure (5, 5'), has been applied by over-growth onto the first zeolite, providing the first porous structure (2, 2').

14. Porous material for catalytic conversion of exhaust gases according to anyone of claims 10-13,

characterized in that the content of oxidation catalyst (OX) has been reduced in outer layers (8) of the first zeolite by means of regulating penetration depth and/or dispersion.

15. Porous material for catalytic conversion of exhaust gases according to any one of claims 10-14,

characterized in that an additional zeolite crystal layer with a reduced content of oxidation catalyst (OX) has been crystallized onto the crystal structure of the first zeolite.

16. Porous material for catalytic conversion of exhaust gases according to any one of claims 10-15,

characterized in that the crystal structure of the first zeolite comprises crystal grains having a grain size (9) and a shape which has been optimized both in order to prevent access for the reducing agent (HC), and in order to allow effective oxidation of NO to NO₂.

17. Porous material for catalytic conversion of exhaust gases according to any one of claims 10-16, characterized in that the first zeolite is a Ferrierite-zeolite or a Chabazite-zeolite.

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18. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-14, characterized in that the reducing agent (HC), which is at least partially consumed according to the third reaction (6), is a hydrocarbon (H_xC_y) and/or a chemical compound ($H_xC_yO_zS_w$) further comprising oxygen and/or sulphur.

10

19. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-18, characterized in that the reduction catalyst is an acidic zeolite catalyst.

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20. Porous material for catalytic conversion of exhaust gases according to any one of claims 2-19, characterized in that the reduction catalyst (RED) comprises Brönstedt acid sites, silver (Ag), copper (Cu), Rhodium (Rh), Indium (In), Iridium (Ir), or combinations of these.

20

21. Porous material for catalytic conversion of exhaust gases according to any one of the preceding claims, characterized in that the oxidation catalyst (OX) comprises platinum (Pt) and/or palladium (Pd).

25

22. Porous material for catalytic conversion of exhaust gases according to any one of the preceding claims, characterized in that the first or/and the second porous structure is/are provided in carriers attached to a substrate (18).

30

35

23. Method for catalytic conversion of exhaust gases, comprising oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO₂) over an oxidation catalyst (OX), according to a first reaction (3), whereby said oxidation catalyst (OX) also has the ability to, according to a second reaction, catalyse oxidation of a reducing agent (HC),

characterized in that the reducing agent (HC) is sterically prevented (4, 4') from coming into contact with the oxidation catalyst (OX), as a result of which primarily the first reaction (3), out of said first and second reactions, takes place over the oxidation catalyst (OX).

24. Method for catalytic conversion of exhaust gases according to claim 23, further comprising a third reaction (6) over a reduction catalyst (RED), wherein nitrogen dioxide (NO₂), in the presence of a reducing agent (HC), is reduced into nitrogen (N₂),

characterized in that the reducing agent (HC) participates in the third reaction (6) and thereby is at least partially consumed, in order to provide catalytically converted exhaust gases (12') having a reduced content of nitrogen monoxide (NO), nitrogen dioxide (NO₂) and the reducing agent (HC), and a proportionately low content of dinitrogen oxide (N₂O) and/or carbon monoxide (CO).

25. Method for catalytic conversion of exhaust gases according to claim 23 or 24,

characterized in that an additional amount (19, 19', 19'') of reducing agent (HC) is added before reduction takes place over the reduction catalyst (RED), according to the third reaction (6).

26. Method for catalytic conversion of exhaust gases according to claim 25,

characterized in that the additional amount (19, 19', 19'') of reducing agent (HC) is regulated on the basis of a measured or previously mapped content (20) of reducing agent (HC) and/or nitrogen oxides (NO_x) in the exhaust gases (12, 12').

27. Method for catalytic conversion of exhaust gases according to claim 26,

characterized in that the measured content (20) of reducing agent (HC) or nitrogen oxides (NO_x) in the catalytically converted exhaust gases (12') is used in a diagnostic control system (22) as a measure of the status of the catalytic conversion.

28. Method for catalytic conversion of exhaust gases according to any one of claims 23-27,

characterized in that the exhaust gases (12), before oxidation over the oxidation catalyst (OX) according to the first reaction (3), are passed through a device having the ability to store and when necessary release nitrogen oxides (NO_x).

29. Method for catalytic conversion of exhaust gases according to any one of claims 23-28,

characterized in that the exhaust gases (12), before oxidation over the oxidation catalyst (OX) according to the first reaction (3), are passed through a device having the ability to store and when necessary release reducing agent (HC).

30. Method for catalytic conversion of exhaust gases according to any one of claims 23-29,

characterized in that the temperature of the exhaust gases is regulated (23) in order to be within an

active temperature interval of the oxidation catalyst (OX) and/or the reduction catalyst (RED).

31. Method for catalytic conversion of exhaust gases according to any one of claims 23-30, characterized in that the at least partially catalytically converted exhaust gases, after (21) oxidation over the oxidation catalyst (OX) and reduction over the reduction catalyst (RED), are allowed to pass a second oxidation catalyst (24) over which oxidation of residues of reducing agent (HC) and/or carbon monoxide can take place.

32. Method for catalytic conversion of exhaust gases according to any one of claims 23-31, characterized in that the exhaust gases (12) originate from an internal combustion engine (25), and that the reducing agent (HC) comprises a hydrocarbon (H_xC_y) and/or a chemical compound ($H_xC_yO_zS_w$) further containing oxygen/and or sulphur.

33. Method for catalytic conversion of exhaust gases according to claim 32, characterized in that both the fuel (26) consumption of the internal combustion engine (25), influencing the chemical composition of the exhaust gases (12), and the residue content of nitrogen oxides (NO_x) in the catalytically converted exhaust gases (12') are regulated in order to fulfil relevant legislative regulations.

34. Method for catalytic conversion of exhaust gases according to claim 32 or 33, characterized in that the internal combustion engine (25) is a diesel engine and that the reducing agent (HC) originates from internal combustion in said diesel engine.

35. Method for catalytic conversion of exhaust gases according to claim 34,

c h a r a c t e r i z e d i n that an additional amount (19) of reducing agent (HC) is added via a fuel injector of the diesel engine and/or via a separate injector for additional reducing agent.

36. Use of a porous material, according to any one of claims 2-22, providing functions both for the oxidation of nitrogen monoxide (NO) into nitrogen dioxide (NO₂) and for the reduction of nitrogen dioxide (NO₂) into nitrogen (N₂), for catalytic conversion of exhaust gases (12) which have an oxygen surplus.

37. Arrangement for catalytic conversion of exhaust gases, whereby said exhaust gases (12) originate from an internal combustion engine (25),

c h a r a c t e r i z e d i n that the arrangement comprises a porous material (1) according to any one of claims 1-22.

38. Arrangement for catalytic conversion of exhaust gases according to claim 37,

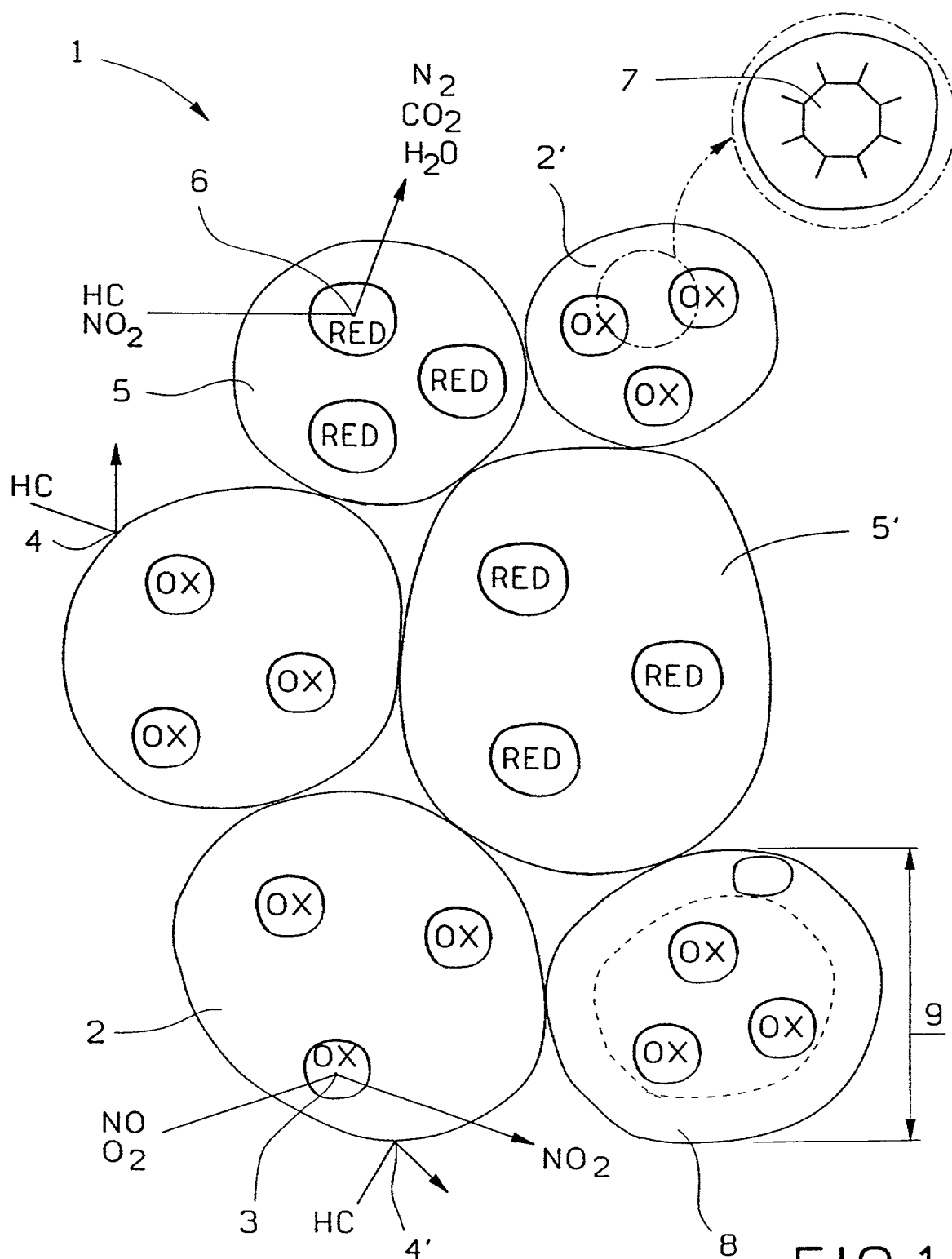
c h a r a c t e r i z e d i n that the arrangement operates through a method according to any one of claims 23-35.

ABSTRACT OF THE DISCLOSURE

Porous materials are disclosed for use in the catalytic conversion of exhaust gases comprising a carrier including a first porous structure, an oxidation catalyst capable of catalyzing the oxidation of NO to NO₂ in the presence of oxygen and catalyzing the oxidation of reducing agent, the oxidation catalyst enclosed within the first porous structure, the first porous structure including pores having dimensions such that the reducing agent is substantially prevented from contacting the oxidation catalyst, whereby the oxidation catalyst primarily catalyses the oxidation of NO to NO₂ as compared to oxidation of the reducing agent during the catalytic conversion of the exhaust gases. Methods for catalytic conversion of exhaust gases using these materials are also disclosed.

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FIG.1

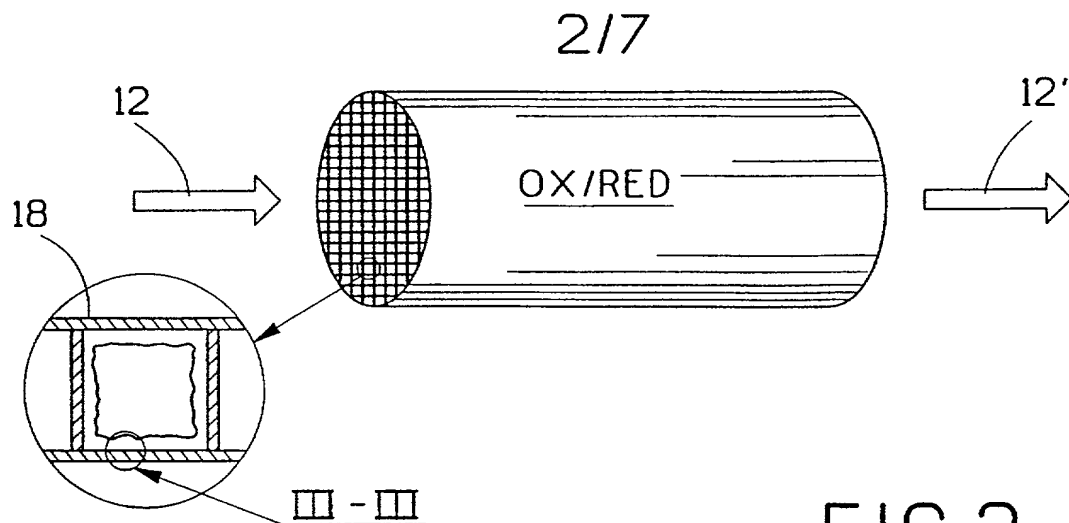


FIG. 2

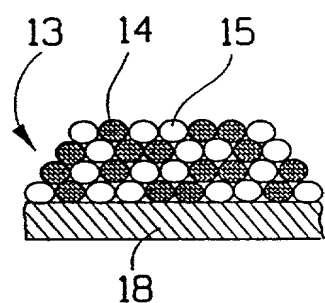


FIG. 3A

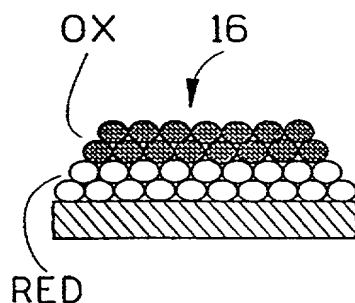


FIG. 3B

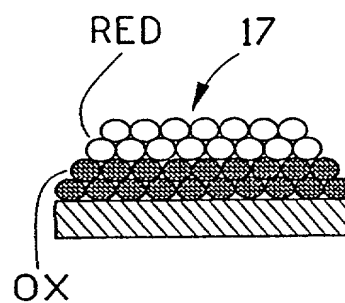


FIG. 3C

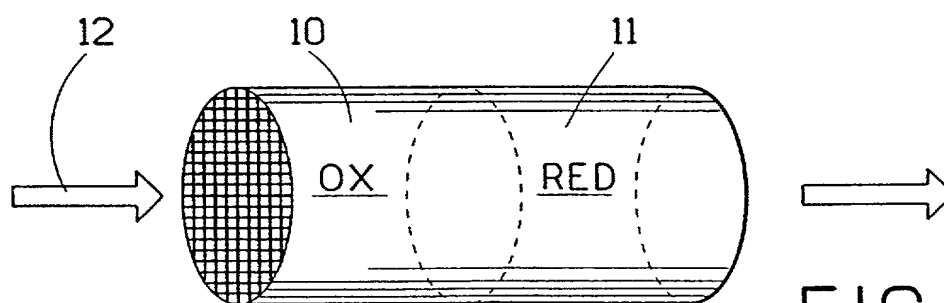


FIG. 4A

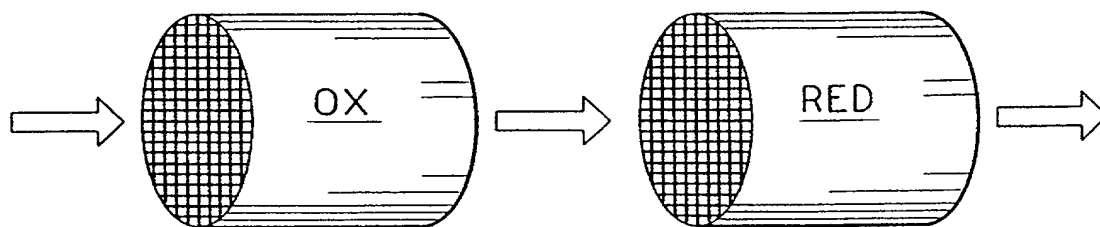


FIG. 4B

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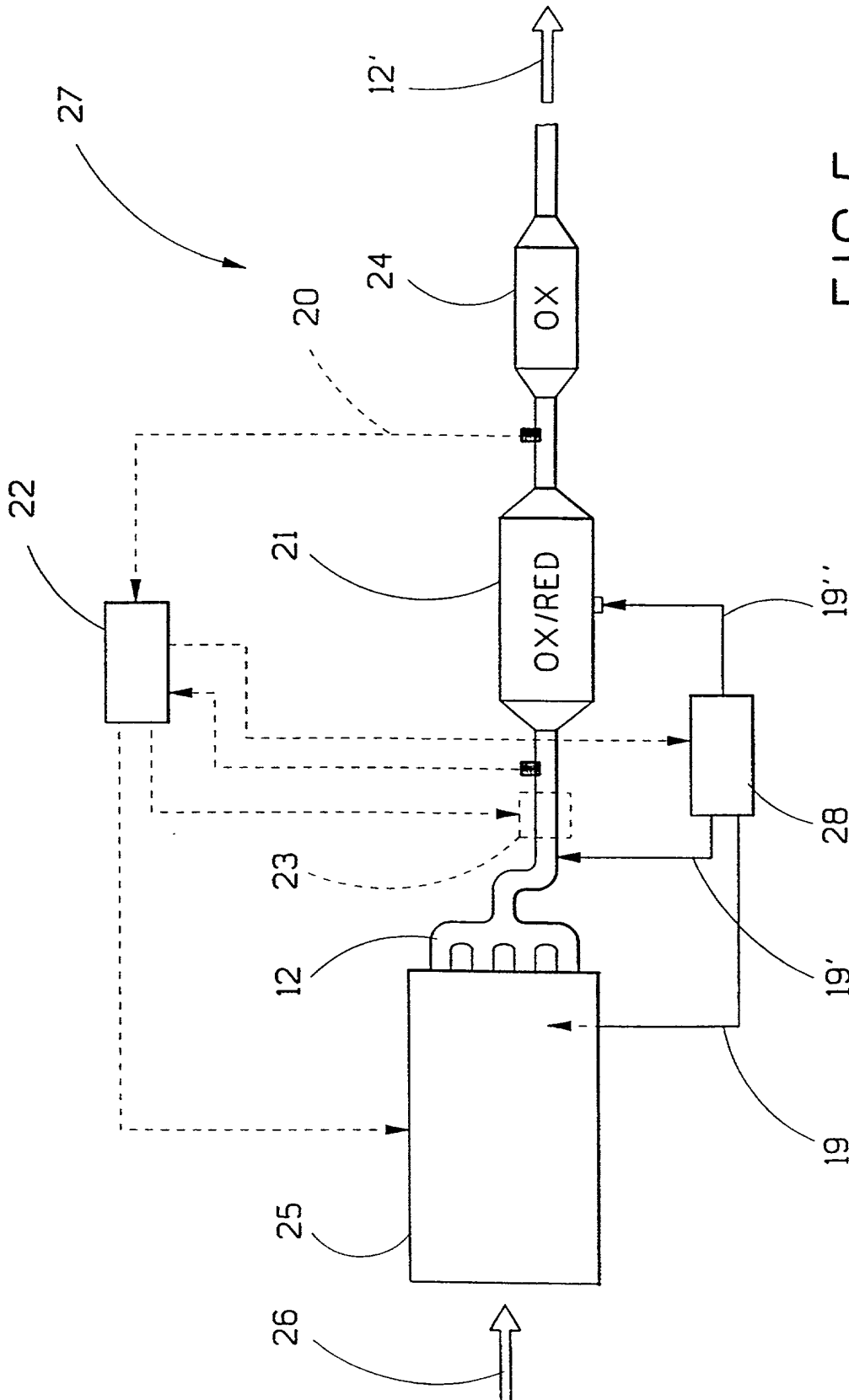
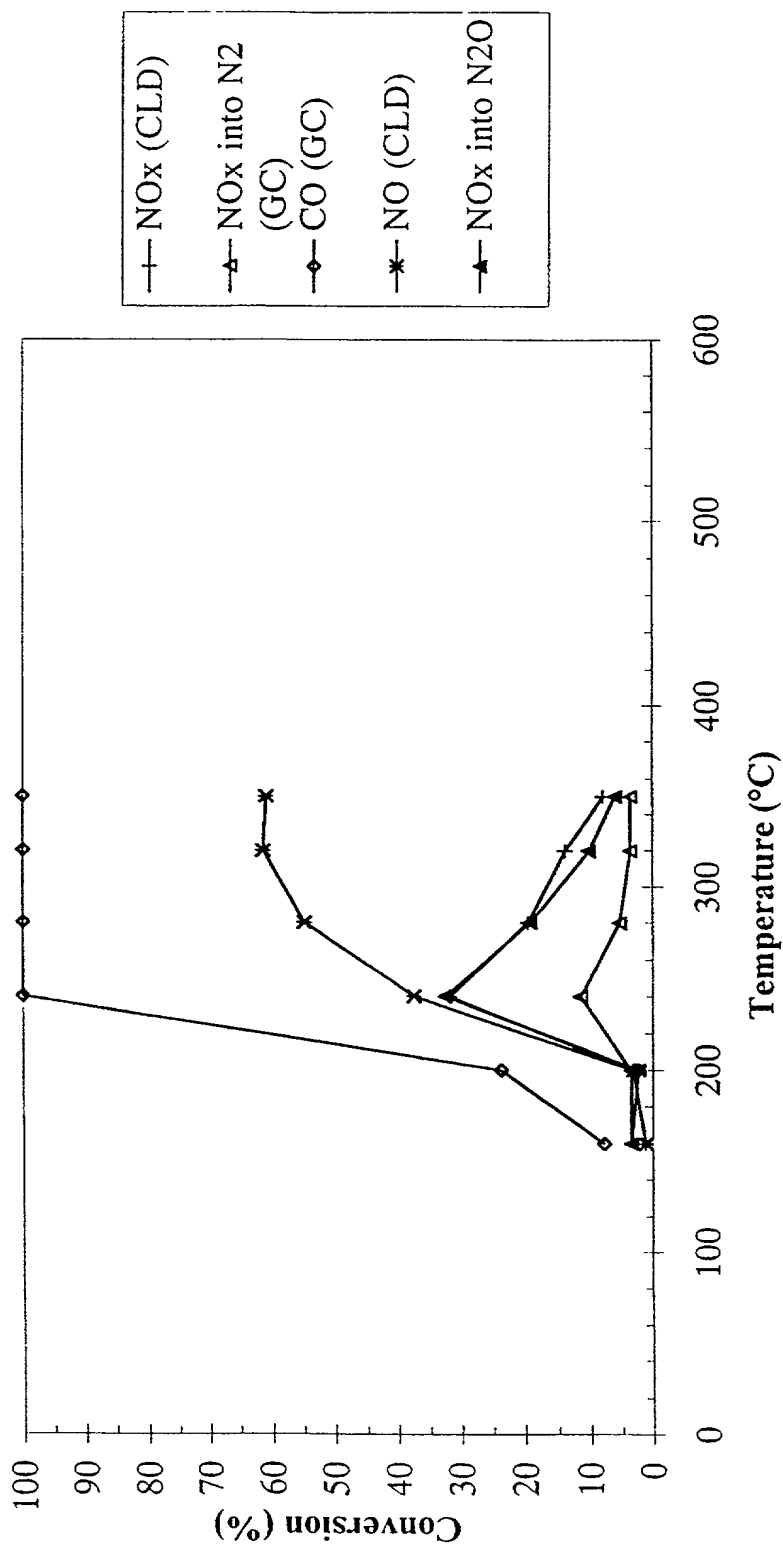


FIG. 5

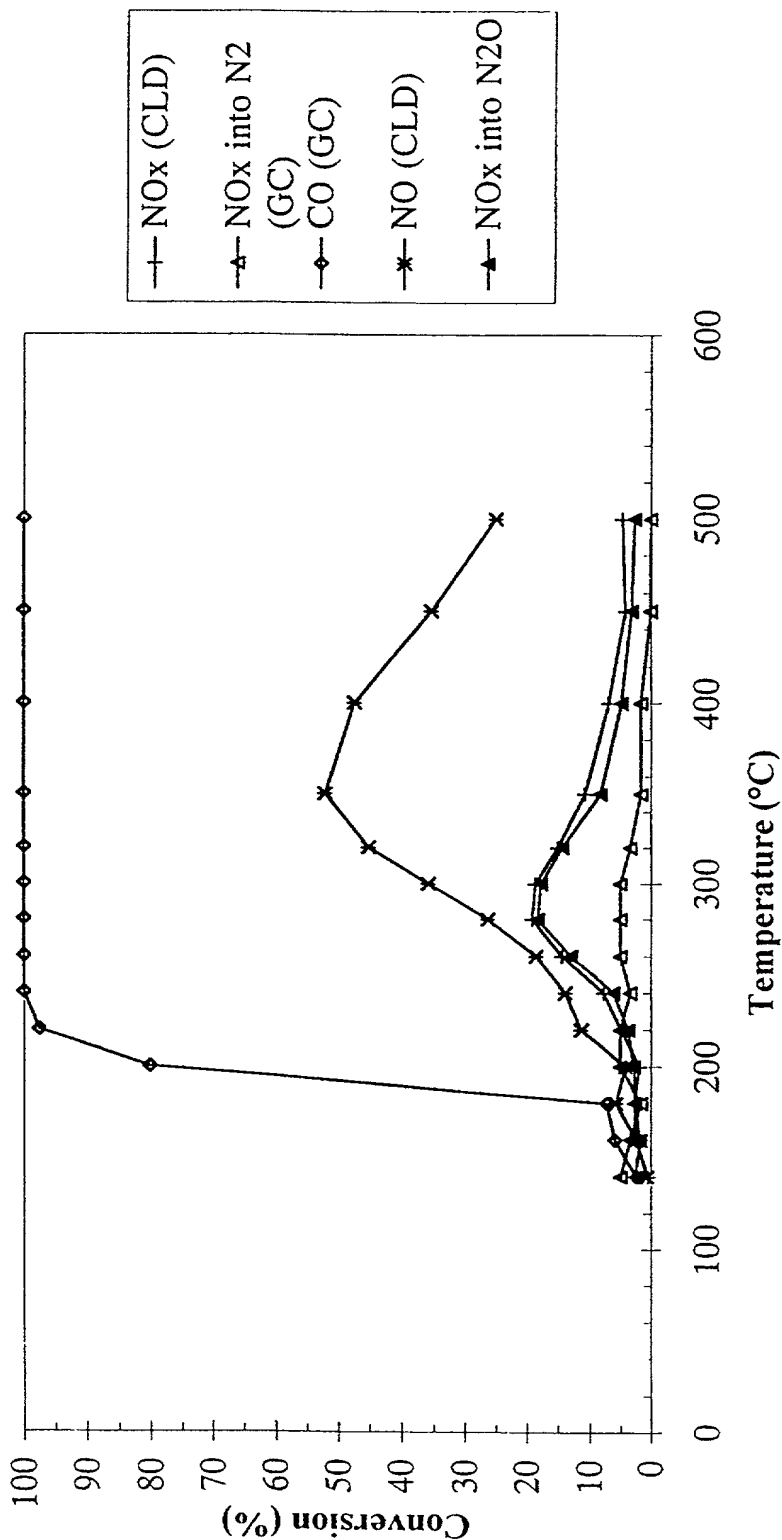
0.5wt% Pt-FER/5wt% Ag-FER (COK-Si/Al=6) (30/70)
(350 ppm C₈H₁₈, 500 ppm NO, VHSV = 60,000 h⁻¹)



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Graph 1B

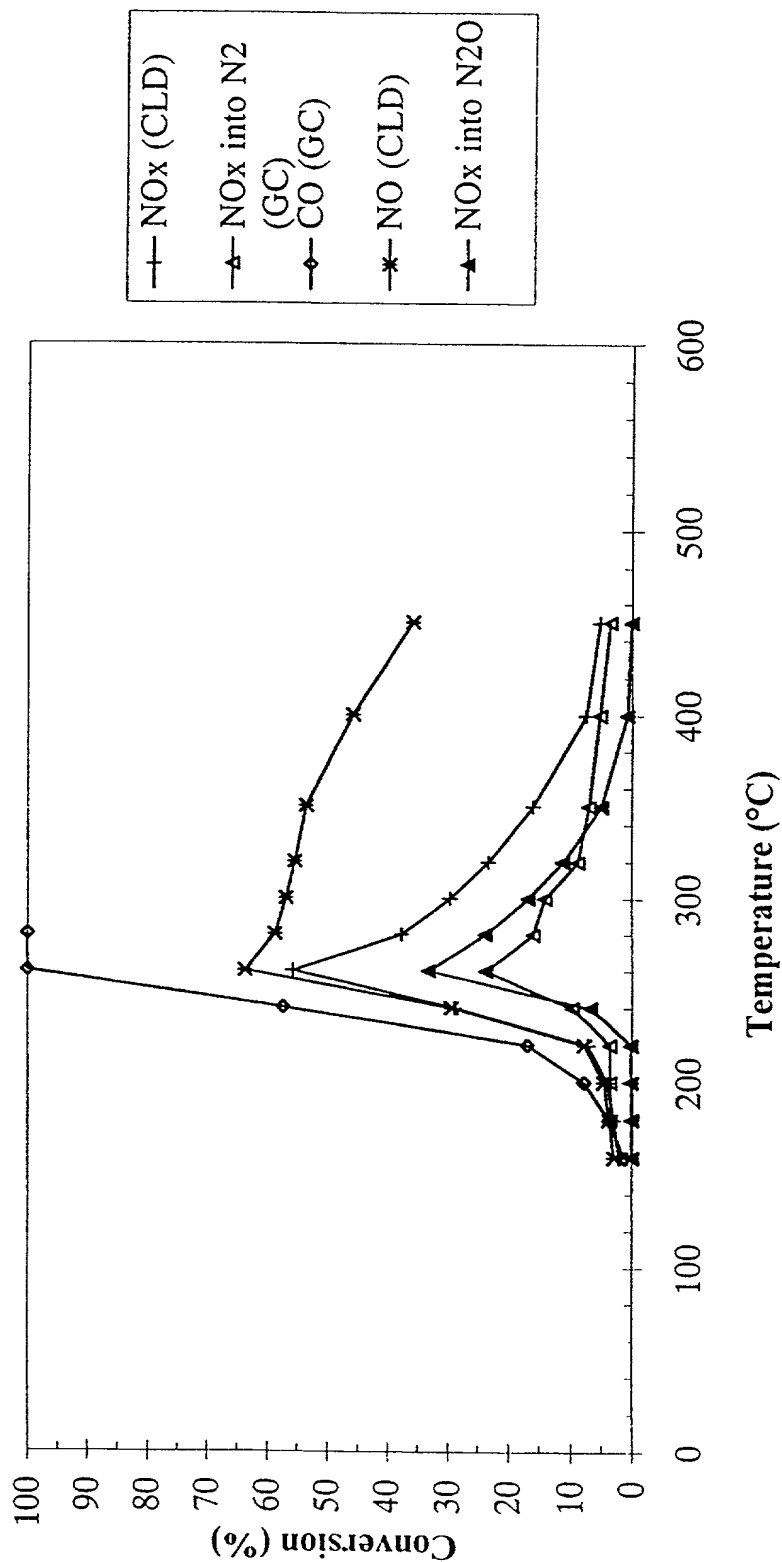
0.5wt% Pt-FER/5Wt% Ag-FER (COK-Si/Al=6) (30/70)
(350 ppm isoC₈H₁₈, 500 ppm NO, VHSV = 60,000 h⁻¹)



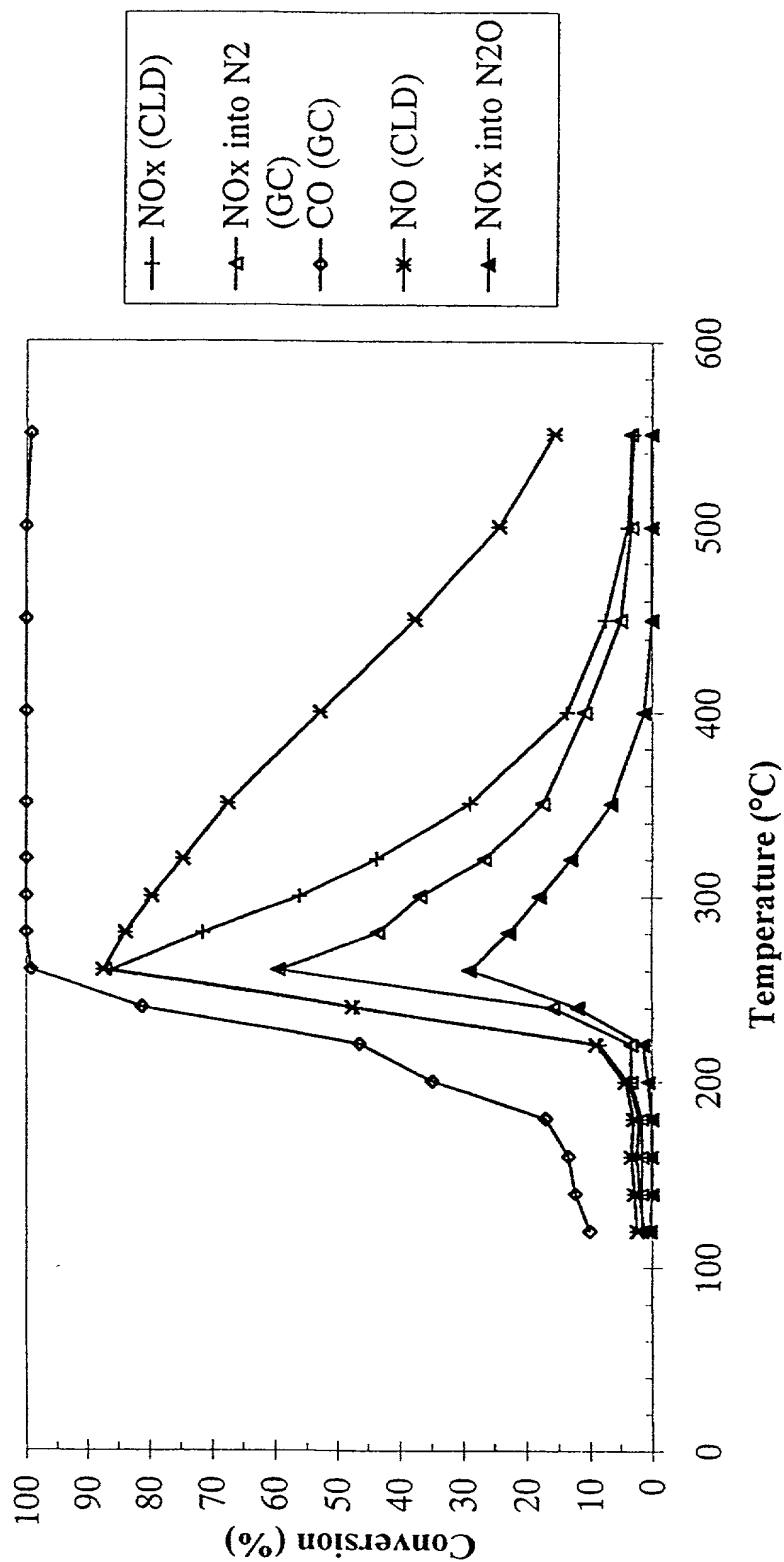
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Graph 2A

0.5wt% Pt-FER/5Wt% Ag-MOR (30/70)
(350 ppm C₈H₁₈, 500 ppm NO, VHSV = 60,000 h⁻¹)



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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

ATTORNEY'S DOCKET NO.: ALBIHN W 3.3-386

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: Porous material, method and arrangement for catalytic conversion of exhaust gases, the specification of which

☐ is attached hereto

☒ was filed on December 10, 1997 as United States Application Number or PCT International Application Number PCT/SE97/02067 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or any PCT international application having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)			
COUNTRY	APPLICATION NUMBER	DATE OF FILING (month, day, year)	PRIORITY CLAIMED
			YES <input type="checkbox"/> NO <input type="checkbox"/>
			YES <input type="checkbox"/> NO <input type="checkbox"/>
			YES <input type="checkbox"/> NO <input type="checkbox"/>

LISTING OF FOREIGN APPLICATIONS CONTINUED ON PAGE 3 HEREOF ☐ YES ☒ NO

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Application Number: _____ Filing Date: _____

Application Number: _____ Filing Date: _____

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Parent Application Serial Number: _____ Parent Filing Date: _____ Parent Patent No.: _____

U.S. Parent Application Serial Number: _____ Parent Filing Date: _____ Parent Patent No.: _____

PCT Parent Number: _____ Parent Filing Date: _____

LISTING OF US APPLICATIONS CONTINUED ON PAGE 3 HEREOF: ☐ YES ☒ NO

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Lawrence I. Lerner, Reg. No. 19,516; Sidney David, Reg. No. 22,768; Joseph S. Littenberg, Reg. No. 20,832; Arnold H. Krumholz, Reg. No. 25,428; William L. Mentlik, Reg. No. 27,108; John R. Nelson, Reg. No. 26,573; Roy H. Wepner, Reg. No. 28,350; Stephen B. Goldman, Reg. No. 28,512; Paul H. Kochanski, Reg. No. 29,660; Marcus J. Millet, Reg. No. 28,241; Bruce H. Sales, Reg. No. 32,793; Daniel H. Bobis, Reg. No. 16,694; Keith E. Gilman, Reg. No. 32,137; Robert B. Cohen, Reg. No. 32,768; Arnold B. Dompier, Reg. No. 29,738; Michael H. Teschner, Reg. No. 32,882; Gregory S. Gewirtz, Reg. No. 36,522; Jonathan A. David, Reg. No. 36,494; Shawn P. Foley, Reg. No. 33,071; Thomas M. Palisi, Reg. No. 36,629; John P. Maidjian, Reg. No. 41,967; Jason D. Shanske, Reg. No. P-43,915; Kimberly V. Flugger, Reg. No. P-43,612; Jason I. Garbell, Reg. No. P-44,1167; Renee M. Robeson, Reg. No. 41,777.

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DECLARATION -- Page 2

ATTORNEY DOCKET NO. ALBIHN W 3.3-386

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1 - ☐ Full name of sole or first inventor (given name, family name): Edward JOBSON

Inventor's signature [Signature] Date Sept. 8, 2000
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Post Office Address: Jägarevägen 5, SE-442 77 ROMELANDA, Sweden

2 - ☐ Full name of second joint inventor, if any (given name, family name): John A. MARTENS

Second Inventor's signature [Signature] Date Sept. 8, 2000
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3 - ☐ Full name of third joint inventor, if any (given name, family name): Anne CAUVEL

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Fourth Inventor's signature [Signature] Date Sept. 8, 2000
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Full name of fifth joint inventor (given name, family name): _____

Fifth Inventor's signature _____ Date _____
Residence: _____ Citizenship: _____
Post Office Address: _____

Full name of sixth joint inventor, if any (given name, family name): _____

Sixth Inventor's signature _____ Date _____
Residence: _____ Citizenship: _____
Post Office Address: _____

Full name of seventh joint inventor, if any (given name, family name): _____

Seventh Inventor's signature _____ Date _____
Residence: _____ Citizenship: _____
Post Office Address: _____

Full name of eighth joint inventor, if any (given name, family name): _____

Eighth Inventor's signature _____ Date _____
Residence: _____ Citizenship: _____
Post Office Address: _____